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Level 1
Environmental Assessment

TRW Systems Group, Redondo Beach, Calif

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IERL-RTP PROCEDURES MANUAL:
LEVEL 1
ENVIRONMENTAL ASSESSMENT

by

J.W. Hamersma, S.L. Reynolds, and R.F. Maddalone

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The manual gives Level 1 procedures (recommended by Industrial Environmental Research Laboratory--Research Triangle Park) for personnel experienced in collecting and analyzing samples from industrial and energy producing processes. The phased environmental assessment strategy provides a framework for determining industry, process, and stream priorities on the basis of a staged sampling and analysis technique. (Level 1 is a screening phase that characterizes the pollutant potential of process influent and effluent streams.) The manual is divided into two major sections: sampling procedures and analytical procedures. The sampling section is further divided into five chapters: fugitive emissions, gases, aerosols, liquids (including slurries), and solids. The analytical section is divided into three chapters: inorganic, organic, and bioassays.

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Analyzing	Slurries	Environmental Assessment		11G
Industrial Processes	Solids		13H	
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PREFACE

The Process Measurements Branch, IERL/RTP, has developed and recommended the implementation of a phased sampling and analytical strategy for Environmental Assessment Programs. The first phase, Level 1, has as its goal the quantification of mass emissions within a factor of 2 to 3 for inorganic elements and organic classes. The second phase, Level 2, has as its goal the quantification and identification of specific compounds. The third phase, Level 3, has as its goal the continuous monitoring of indicator compounds as surrogates for a large number of specific compounds.

This document represents the first time that a set of integrated sampling and analytical procedures for environmental assessment programs has been compiled. As such, it is anticipated that many readers might take exception with specific sampling and/or analytical tools; however, we feel that the recommended environmental assessment system is both valid and information effective.

IERL/RTP Contractors or Grantees will use the system described in this document for Environmental Assessment Programs. It is anticipated that non-IERL/RTP organizations who are active in the environmental assessment field will also utilize this manual.

This manual has been made as specific as possible, although it is recognized that it is impossible to specify the exact sampling and analysis procedure for every possible circumstance. When situations arise where alternative Level 1 sampling and analysis procedures are necessary or desired, the contractor is directed to submit his alternate plan to his project officer and the Process Measurements Branch, IERL-RTP, Research Triangle Park, for approval before actual work is initiated.

If this document becomes universally implemented, then sets of comparable data will be generated and prioritization of the environmental insults associated with differing processes can be made.

James A. Dorsey
Chief, Process Measurements Branch

ABSTRACT

This manual gives Level 1 procedures (recommended by Industrial Environmental Research Laboratory--Research Triangle Park) for personnel experienced in collecting and analyzing samples from industrial and energy producing processes. The phased environmental assessment strategy provides a framework for determining industry, process, and stream priorities on the basis of a staged sampling and analysis technique. Level 1 is a screening phase that characterizes the pollutant potential of process influent and effluent streams.

The manual is divided into two major sections: sampling procedures and analytical procedures. The sampling section is divided into five chapters: fugitive emissions, gases, aerosols, liquids (including slurries), and solids. The analytical section is divided into three chapters: inorganic, organic, and bioassays.

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INTRODUCTION

This procedures manual has been prepared for the Industrial and Environmental Research Laboratory of the Environmental Protection Agency, Research Triangle Park, North Carolina.

It is written so that the sampling and analysis professional can plan and execute the sampling and analytical portion of a source assessment program. This manual is not intended for use by an inexperienced professional staff or by technicians. Analysis procedures are included as schemes with descriptions for all the samples obtained by the methods delineated in Chapters II through VI. For those samples which are analyzed as part of the sampling procedure and for those samples which must be analyzed on-site, reference is made to analysis both in the sampling and appropriate analysis chapters.

The sampling procedures in this manual are designed to be an integral part of the phased environmental assessment and apply primarily to Level 1. The purpose of this initial effort is to obtain preliminary environmental assessment information, identify problem areas, and provide the basis for the prioritization of streams, components and classes of materials for further consideration in the overall assessment. As such, the results of the sampling and of the corresponding analysis procedures are quantitative within a factor of ± 2 to 3. A detailed discussion of the approach along with the criteria used for method selection is given in Chapter I.

In the preparation of this manual applicable sampling literature was reviewed and a set of appropriate sampling procedures for each of five sampling categories was then defined. Included in these procedures are criteria for sample site selection, sampling equipment and manpower requirements, amount of sample required, and special sample preservation techniques. Samples for which on-site analyses are necessary are identified along with the appropriate procedures.

Chapters II through VI of this manual center around five different types of Level 1 sampling activities that can be found in most industrial complexes: gas and vapor samples, gaseous streams containing particulate matter, fugitive emissions sampling, liquid and slurry sampling, and solids sampling. In this way, the complex and difficult task of organizing the manpower and equipment necessary for a successful field test is facilitated. Each chapter also includes sections on the general problem, preparations needed for the tests, sampling procedures, and on-site analysis or packaging of samples for shipment.

Chapters VII specify a Level 1 analysis scheme along with a description of the analysis for each of the sample types described. These three chapters are entitled: Analysis of Inorganic Materials, Analysis of Organic Materials, Particulate Morphology and Identification, and Biological Testing. The schemes identify the methods of analysis, anticipated output and predicted level of effort required to implement each analysis scheme.

This manual also identifies the ancillary process data required to estimate mass emission rates, emission rates per unit of products or other calculations necessary for an environmental assessment. The accuracy requirements are consistent with the Level 1 environmental assessment philosophy.

This manual has been made as specific as possible, although it is recognized that it is impossible to specify the exact sampling and analysis procedure for every possible circumstance. When situations arise where alternative Level 1 sampling and analysis procedures are necessary or desired, the contractor is directed to submit his alternate plan to his project officer and the Process Measurements Branch, IERL-RTP, Research Triangle Park, for approval before actual work is initiated.

CHAPTER I

STRATEGY AND GENERAL INFORMATION

The Process Measurements Branch of IERL/RTP has developed a three-tiered or phased approach to performing an environmental source assessment. In this phased approach, three distinctly different sampling and analytical activities are envisioned. While each of the three phases is briefly described in Section 1.1, this procedures manual focuses on the Level 1 sampling and analysis effort.

This manual describes for an experienced professional a set of sampling and analytical procedures which are compatible with the information requirements of a comprehensive Level 1 environmental assessment. This manual is not intended for use by inexperienced personnel. A comprehensive environmental assessment involves multimedia environmental source sampling. The techniques described in Chapters II through VI will provide an adequate sample of fugitive air and water emissions, ducted air and water emissions, liquids and slurries, and solids for the analyses described in Chapters VII through X. The overall sampling and analysis effort is designed to be quantitiative in nature with an overall accuracy of a factor of 2 to 3.

1.1 DEFINITION OF STRATEGIES

The phased sampling and analytical strategy was developed to focus available resources (both manpower and dollars) on emissions which have a high potential for causing measurable health or ecological effects, and to provide comprehensive chemical and biological information on all sources of industrial emissions. Discussions of this philosophy, the information-cost benefits, and a summary of the application of the phased approach to sampling and analysis follow.

1.1.1 The Phased Approach

The phased approach requires three separate levels of sampling and analytical effort. The first level utilizes quantitative sampling and analysis procedures accurate within a factor of 2 to 3 and: 1) provides preliminary environmental assessment data, 2) identifies problem areas, and 3) formulates the data needed for the prioritization of energy and industrial processes, streams within a process, components within a stream, and classes of materials for further consideration in the overall assessment. The second, Level 2, sampling and analysis effort, after having been focused by Level 1, is designed to provide additional information that will confirm and expand the information gathered in Level 1. This information will be used to define control technology needs and may, in some cases, give the probable or exact cause of a given problem. The third phase, Level 3, utilizes Level 2 or better sampling and analysis methodology in order to monitor the specific problems identified in Level 2 so that the critical components in a stream can be determined exactly as a function of time and process variation for control device development.

1.1.2 Strategy of the Phased Approach

The phased approach recognizes that it is impossible to prepare for every conceivable condition on the first sampling or analysis effort. In some cases, unknown conditions and components of streams will result in unreliable information and data gaps that will require a significant percentage of the sampling or analysis effort to be repeated.

There is a possibility that many streams or even the entire installation may not be emitting hazardous substances in quantities of environmental significance. Conversely, certain streams or sites may have such problems that a control technology development program can be initiated in parallel with a Level 2 effort. If either of these situations could be determined by a simplified set of sampling and analysis techniques, considerable savings could result in both time and funds.

A second possibility is that budgetary limitations may require prioritizing a series of installations so that the available funds can be used in assessing those installations most in need of control technology. Here again, a simplified sampling and analysis methodology would be advantageous to the overall environmental assessment effort.

The phased approach offers potential benefits in terms of the quality of information that is obtained for a given level of effort and in terms of the costs per unit of information. This approach has been investigated and compared to the more traditional approaches (Ref. 1) and has been found to offer the posibility of substantial savings in both time and funds required for assessment.

The three sampling and analysis levels are closely linked in the overall environmental assessment effort. Level 1 identifies the questions that must be answered by Level 2, and Level 3 monitors the problems identified in Level 2 to provide information for control device design and development. For example, if a Level 1 test indicated that polycyclic organic material (POM) might be present in significant amounts and gave a positive mutagenicity test, Level 2 sampling and analysis would be designed to determine the exact quantities of organic constituents, the percentage of POM, and the identity of as many specific POM compounds present as economically possible. In addition, using the Level 1 data and any available Level 2 results, the sample would be retested for cytotoxicity and mutagenicity in order to confirm and expand the total bioassay information. A test for carcinogenicity would also be run if the results of these tests are positive. The entire data package could then be used to design the control technology research and development needs for the stream in the Level 3 effort.

A detailed explanation of Level 1 and Level 2 sampling and analyses along with their expected outputs is given in the following sections. Because Level 3 sampling and analysis is totally process-and even site-specific, neither a general approach nor sampling and analysis methodologies can be specified and for this reason, Level 3 will not be discussed further.

1.1.2.1 Definition of Level 1 Sampling and Analysis

The Level 1 sampling and analysis goal is to identify the pollution potential of a source in a quantitative manner with a target accuracy factor of ±2 to 3 (0.3). At the initiation of an environmental assessment, little is known about the specific sampling requirements of a source both practically and technically, and hence the emphasis is on survey tests.

For this reason, no special procedure is employed in obtaining a statistically representative sample and the chemical, physical, and biological testing has survey and/or quantitative accuracy consistent with the characteristics of the sample.

At this level, the sampling and analysis is designed to show within broad general limits the presence or absence, the approximate concentrations, and the emission rate of inorganic elements, selected inorganic anions, and classes of organic compounds. The particulate matter is further analyzed through size distribution as well as microscopic examination in order to determine gross physical characteristics of the collected material. Biotesting is designed to obtain information on the human health effects and biological effects of the sample.

The results of this phase are used to establish priorities for additional testing among a series of energy and industrial sources, streams within a given source, and components within streams. Level 1 has as its most important function the focusing of sampling and analysis programs on specific streams and components for the Level 2 effort. It delineates specific sampling, analysis and decision-making problem areas, and directs and establishes the methodology of the Level 2 effort so that additional information needs can be satisfied. If it can be proven that equivalent Level 1 data exist for all streams of interest, then a Level 1 effort need not be conducted. If partial data exists, Level 1 must be performed on all streams.

Another possible exception to the strict adherence to the Level 1 technique involves the application of slightly more sophisticated procedures where specific pollutants of high current interest are concerned. In this case, the approach would involve a more complex Level 2 sampling and/or analytical strategy in the initial Level 1 plan.

1.1.2.2 Definition of Level 2 Sampling and Analysis

The Level 2 sampling and analysis goal is to provide definitive data required in the environmental assessment of a source. The basic questions to be answered and major problem areas have been defined in Level 1 for maximum cost and schedule efficiency. Consequently, Level 2 sampling and analysis is characterized by obtaining statistically representative samples, accurate stream flow rates, and by identification and quantification of specific organic species and/or classes and inorganic elements and/or species. Biotesting in selected areas is expanded.

Although Level 2 sampling and analysis require the use of methodology considerably more complex than that used in Level 1, it will not always be true that a Level 2 effort at a given site will be more manpower intensive than the Level 1 effort. In many cases, the Level 1 effort will so thoroughly delineate the streams and components of these streams of interest that the Level 2 effort may be less costly than the Level 1 effort. Some possible cases are:

- A flue gas source where volatile organic components were the only materials found in a sample which were of environmental interest; thus additional samples would be needed for complete analysis. The additional samples could be taken using a simple organic sampling train operated by one man out of a car instead of the SASS train operated by a crew from a van.
- A source where the only stream of interest is an ash or refuse stream with significant leachable inorganic elements of environmental interest. On Level 2, a representative sample would be taken and accurately analyzed only for the elements of interest.
- A fugitive emissions problem which can be defined by conventional instruments and a meteorological station operated from a conventional van.
- A source emitting particulate matter of which only one or two size fractions are significant or of interest for either organic components or specific trace inorganic elements.
- A source that only has a water problem, and either organic components or trace inorganic elements must be analyzed and the stream monitored for accurate flow rates.
- A source where trace inorganic elements are found at generally low enough levels where they are not of environmental significance. The fuel or other raw materials may be monitored to establish that the inorganic constituents are never input at levels high enough to cause an environmental problem.

Level 2 would thus provide sufficient detailed information concerning the problems delineated by Level 1 such that control stream priorities, total environment insult, and an initial estimate of process/control system regions of overlap can be established.

1.2 MULTIMEDIA SAMPLING PROCEDURES

The Level 1 procedure described in this manual can be utilized to acquire process samples, effluent samples, and feed stock samples. The Level 1 environmental assessment program must, at a minimum, acquire a sample from each process feed stock stream, from each process effluent stream, and of fugitive air/water emissions. The feed streams data are necessary to establish a baseline for comparison. The effluent stream sampling program is required to determine the mass emissions rate and the environmental insult which will result. Sampling and analytical procedures which are required to support in comprehensive environmental source assessment must be multimedia in nature.

1.2.1 Classification of Streams for Sampling Purposes

The basic multimedia sampling strategy shown in overview form in Figure 1 has been organized around the five general types of sampling found in industrial and energy producing processes rather than around the analytical procedures that are required on the collected samples. This facilitates the complex and difficult task of organizing the manpower and equipment necessary for successful field sampling and establishing meaningful units of cost.

The five sample types are:

- Gas/Vapor – These are samples for light hydrocarbon and inorganic gas analysis. They include samples from input and output process streams, process vents, and ambient air.
- Liquid/Slurry Streams – Liquid streams are defined as those containing less than 5 percent solids. Slurries are defined as those containing greater than 5 percent solids. Non-flowing pastes are considered solids.

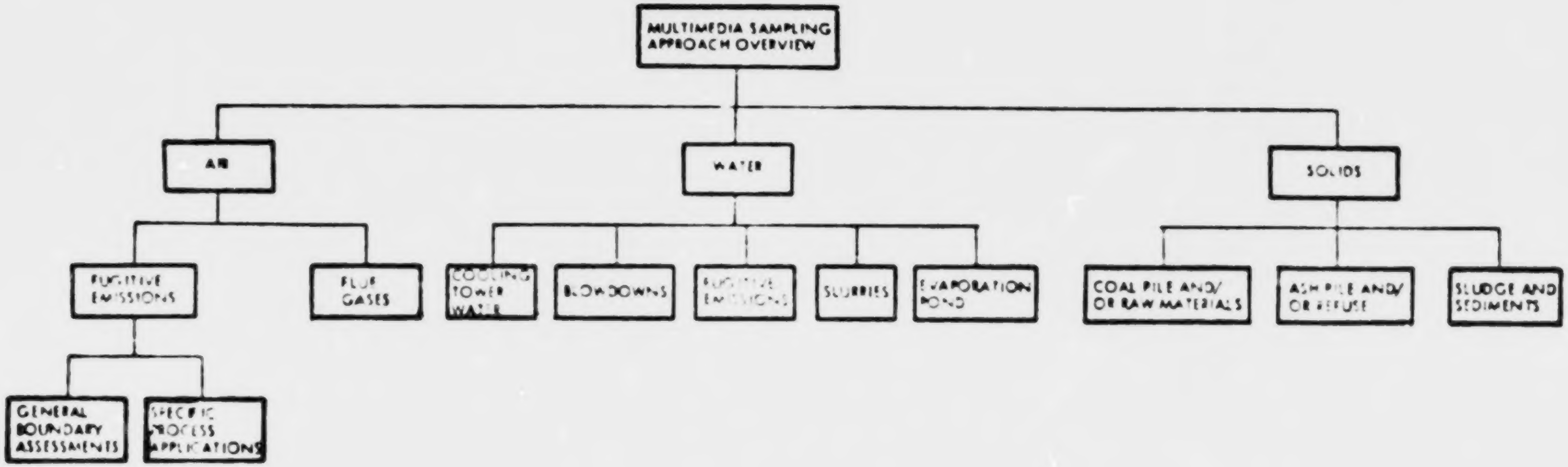


Figure 1. Multimedia Sampling Approach Overview

- Solids - These include a broad range of material sizes from large lumps to powders and dusts, as well as non-flowing wet pastes. Because the distinction between solids and slurries can become blurred, the reader should consult both Chapters V and VI when in doubt.
- Particulate or Aerosol Samples - This involves sampling in contained streams such as ducts or stacks.
- Fugitive Emissions These are gaseous and/or particulate emissions from the overall plant or various process units.

Flow diagrams which show the overall relationship of the samples to the analysis scheme are shown in Figures 2 and 3.

1.2.2 Phased Approach Sampling Point Selection Criteria

The selection of sampling points in processes where phased level sampling techniques are employed relies on the concept previously stated: that Level 1 sampling is oriented towards obtaining quantitative data with relaxed accuracy requirements for determination of the pollution potential of a source, whereas Level 2 sampling is intended to acquire more accurately the data necessary for a definitive environmental assessment on prioritized streams. Stream parameters such as flow rates, temperature, pressure, and other physical characteristics will be obtained on both levels within the accuracy requirements of a given level of sampling. For example, a Level 1 particulate matter sample is obtained at a single point under pseudoisokinetic conditions. This means that the sample is acquired at the point of average velocity which has been determined by a velocity traverse taken at typical points in the stream. The sample is withdrawn by means of a flow rate through the SASS Train Cyclones (see Chapter III) by using a probe nozzle which is specifically selected for isokinetic conditions; however, this flow rate must not be allowed to change since a change in flow rate will alter the particle cutoff efficiency of the cyclone system. In Level 2, however, where quantitative data are required, isokinetic samples must be withdrawn using a full traverse with a port in specific locations away from ducting bends and other obstructions in order to ensure a sample representative of the actual effluent. The recommendations in this manual are restricted to Level 1 sampling and analysis criteria only.

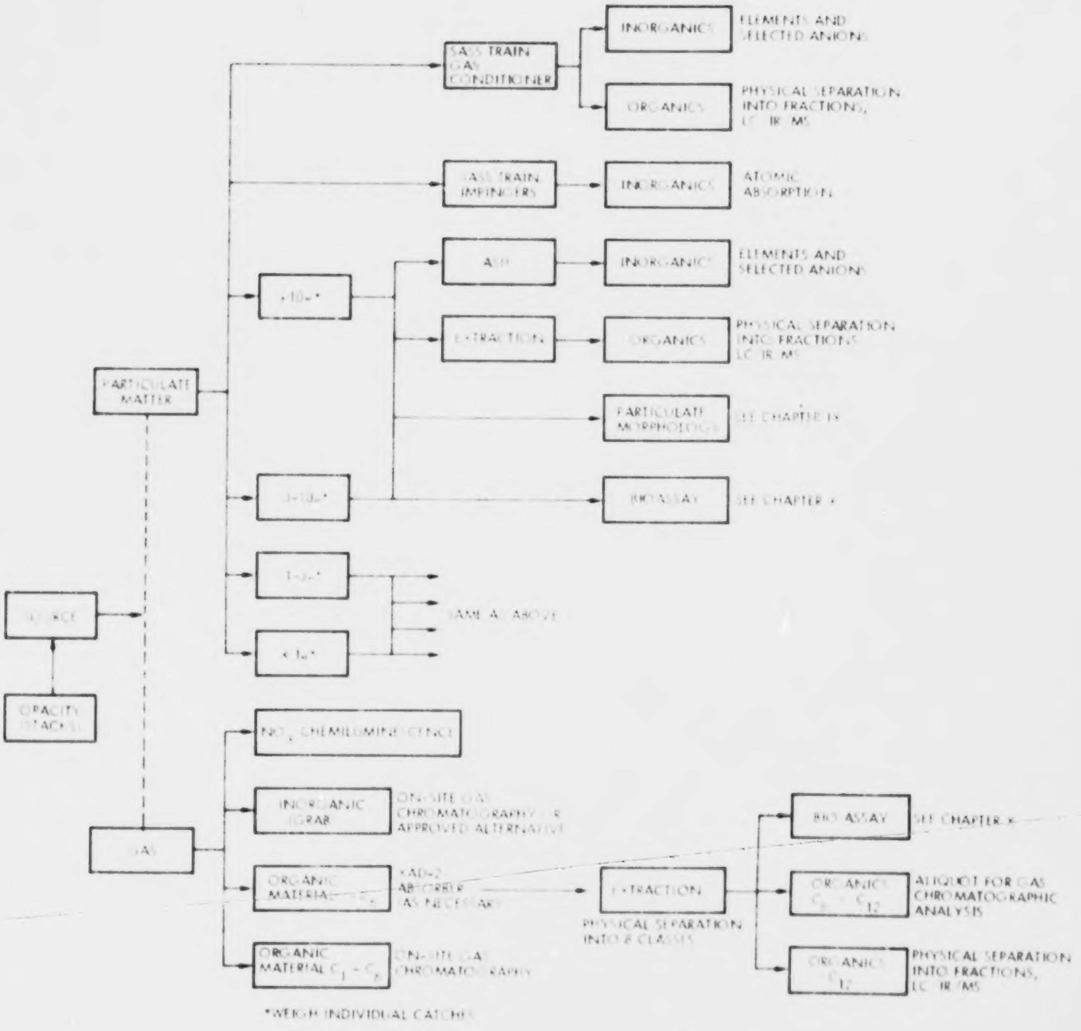

INORGANICS
ELEMENTS AND SELECTED ANIONS
SASS TRAIN GAS CONDITIONER
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS, LC IR MS
SASS TRAIN IMPINGERS
INORGANICS
ATOMIC ABSORPTION
ASH
INORGANICS
ELEMENTS AND SELECTED ANIONS
>10μ*
EXTRACTION
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC IR MS
PARTICULATE MATTER
PARTICULATE MORPHOLOGY
SEE CHAPTER IX
3-10μ*
BIOASSAY
SEE CHAPTER X
1-3μ*
SAME AS ABOVE
SOURCE
<1μ*
OPACITY (STACKS)
NO_x CHEMILUMINESCENCE
INORGANIC (GRAB
ON-SITE GAS CHROMATOGRAPHY OR APPROVED ALTERNATIVE
BIO ASSAY
SEE CHAPTER X
GAS
ORGANIC MATERIAL > C6
XAD-2 ABSORBER (AS NECESSARY)
EXTRACTION
PHYSICAL SEPARATION INTO 8 CLASSES
ORGANICS C6 - C12
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS
ORGANIC MATERIAL C1 - C6
ON-SITE GAS CHROMATOGRAPHY
ORGANICS > C12
PHYSICAL SEPARATION INTO FRACTIONS, LC IR MS
*WEIGH INDIVIDUAL CATCHES

Figure 2. Basic Level 1 Sampling and Analytical Scheme for Particulates and Gases

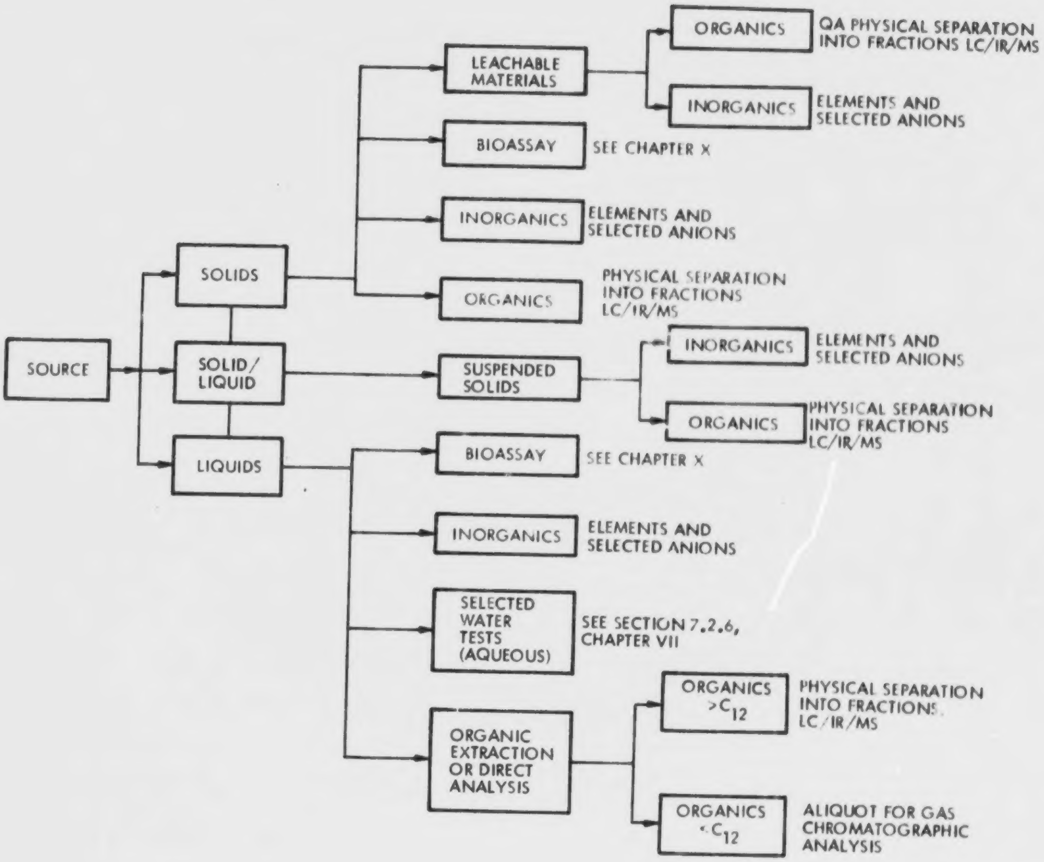

SOURCE
SOLIDS
SOLID/ LIQUID
LIQUIDS
LEACHABLE MATERIALS
ORGANICS
QA PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
INORGANICS
ELEMENTS AND SELECTED ANIONS
BIOASSAY
SEE CHAPTER X
INORGANICS
ELEMENTS AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
SUSPENDED SOLIDS
INORGANICS
ELEMENTS AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
BIOASSAY
SEE CHAPTER X
INORGANICS
ELEMENTS AND SELECTED ANIONS
SELECTED WATER TESTS (AQUEOUS)
SEE SECTION 7.2.6, CHAPTER VII
ORGANIC EXTRACTION OR DIRECT ANALYSIS
ORGANICS >C12
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
ORGANICS <C12
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS

Figure 3. Basic Level 1 Sampling and Analytical Scheme for Solids, Slurries and Liquids

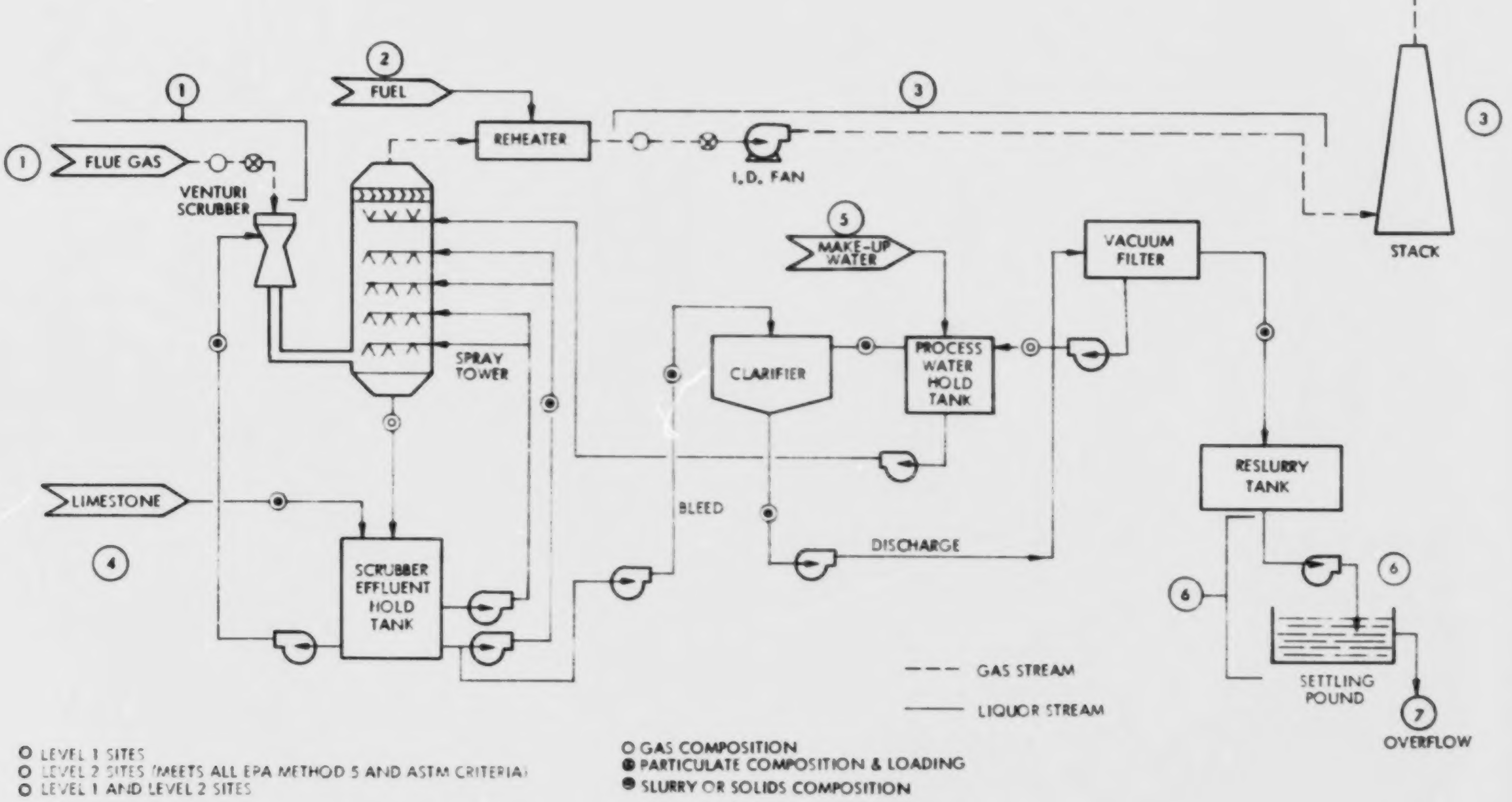
Similar considerations apply to site selection for sampling liquids and solids. On Level 1, liquid samples can be taken from tanks or other containers without depth integration and from pipes using a simple tap sample rather than using a multiported probe to take a time integrated sample. In slurry streams, an effort should be made to sample a turbulent or well mixed area, but this and other requirements can be relaxed considerably for Level 1 site selection.

In the case of solids sampling, the standard procedures used in sampling piles and stationary containers are relaxed on Level 1 both by taking fewer increments to make a composite and by relaxing or eliminating the requirements for depth integrated sampling. For moving solid streams, a simplified sample is obtained by reducing or eliminating the number of increments required for the time averaging aspect of the sampling procedure.

In most cases, Level 1 sampling methods generally encompass approved standard EPA, ASTM, and API techniques. Modifications are then made to these techniques to adapt them to the time and cost constraints consistent with the Level 1 sampling philosophy. These modifications include: 1) reducing port selection criteria; 2) eliminating the requirements for traversing, continuous isokinetic sampling, and replicate sampling in the collection of particulate matter; and 3) use of grab samples for ambient, water, and solid samples. Using these sampling point selection criteria, a sampling point selection model illustrating Levels 1 and 2 sampling points as developed in another program (Ref. 1) is shown in Figure 4 for a wet limestone spray tower system installed at Paducah, Kentucky.

1.2.3 Stream Prioritization Using the Phased Approach

Industrial and energy producing processes are highly complex systems consisting of a wide variety of interrelated components. Level 1 sampling will show that many influent and effluent streams have no environmentally significant impact. These data can be used to reduce the number of samples required for Level 2 substantially, and can permit reallocation of resources. Thus, comprehensive stream prioritization based on the Level 1 sampling and analysis effort will identify streams with widely varying environmental priorities. In many cases, the Level 1 information will be sufficient to



* THE POWER PLANT IS NOT INCLUDED FOR THE PURPOSES OF THIS REPORT.

Figure 4. Typical Process Flow Diagram for Limestone Venturi Spray Tower System

eliminate certain streams entirely from the Level 2 effort. In other cases, limited resources may require the omission of certain low priority streams.

1.3 DATA REQUIREMENTS AND PRE-TEST PLANNING (Ref. 1, 2, 3, 4, 5, 6)

The final decision to test a particular plant will be the result of the prioritization studies and of the preliminary selection process based on the site selection criteria of a given program, and on the data requirements of the overall program or general EPA objective.

Before the actual sampling and analysis effort is initiated, the data requirements must be established and used to help identify test requirements as well as any anticipated problems. The following paragraphs present a general summary of these requirements and planning function which must be applied or expanded to meet the needs of the individual tests to be performed. Specific recommendations concerning data requirements associated with each of the process streams are discussed in the appropriate chapters of this manual.

1.3.1 Process Data Needs

Before traveling to a plant for a pre-test site survey, it is necessary to become familiar with the process used at the site. This involves understanding the chemistry and operational characteristics of the various unit operations as well as any pollution control processes. It is particularly important to know that detailed relevant process data are necessary for the sampling and analysis effort as well as for the overall environmental assessment. The reasons for this are:

1) From a knowledge of the process and the composition of input materials and products, conclusions about pollutants likely to be found in waste streams can be drawn

2) One must know where to look for waste streams, including fugitive emissions

3) One must know how plant operating conditions are likely to affect waste stream flow rates and compositions

4) Thorough familiarity with the process permits design of a proper sampling programs

5) Thorough knowledge of the interrelationships among process variables permits extrapolation to conditions in other sizes of the system being assessed, and

6) Detailed process data are the basis from which control technology development programs proceed, should environmental assessments indicate such need.

Familiarization with the process is also necessary so that a checklist of the requisite data can be developed, including temperatures, pressures, flow rates, and variations of conditions with time for the pre-test site survey.

For any given sampling and analysis task, the data collected must be consistent with the overall Level 1 objectives. Thus, the minimum amount of data for a given stream is flow rate per unit time at a given temperature and pressure. Additional data that may be necessary are average flow per unit time, the effect of process variations on stream flow and composition, and normal variations in flow and compositions with variations in process cycling. Appendix A contains a checklist of appropriate data that may be collected. It is expected that professional sampling and analysis personnel in conjunction with the EPA Project Officer and PMB-IERL-RTP will select the appropriate data requirements for a given industry.

1.3.2 Pre-test Site Survey

After establishing the necessary process data needs and selecting a tentative set of sampling points, a pre-test site survey should be performed. At the test site, the survey team should meet with the plant engineer to verify the accuracy of the existing information and arrange for the addition of any missing data. Using this information, the survey team will then proceed to select the actual sampling sites with the following criteria in mind:

- The sampling points should provide an adequate base of data for characterizing the environmental impact of the source on the environment within a factor of 2 to 3.
- When possible, each sampling point should provide a representative sample of the effluent streams. (This is a desirable but not a strict requirement of Level 1 sampling).

- The sampling site must have a reasonably favorable working environment. The survey personnel must consider the temperature and noise level in the sampling areas, if protection from rain or strong winds exists, and whether safe scaffolding, ladders, pulleys, etc., are present.

The identification of support facilities and services is an essential aspect of the site survey. In an effort to minimize the requests made upon the operators and scheduling problems for these support services, it is desirable that the test van operate completely independently of external support facilities. The large electrical power requirements of the test van and the sometimes limited electrical power availability at many industrial/commercial sites make it important that the van carry sufficient electric generating capacity to operate all test and support equipment. The van should also carry a water tank for essential services. Where available, electrical power and water services may be connected for auxiliary service. These and other specific mobile laboratory fabrication requirements for Level 1 sampling and analysis are presented in Appendix B.

The results of the pre-test site survey must be sufficiently detailed so that the field test problem of sampling the correct process stream at the proper sampling location and using the appropriate methodology will be completely defined prior to arrival of the field test team at the source site.

1.3.3 Pre-test Site Preparation

Since in most cases the manpower requirements for site preparation are usually low to moderate, a relatively low effort was assumed for site preparation, under the assumption that major modifications required in extreme cases are out of the scope of this manual.

Thus, it was assumed that the erection of scaffolding and the provision of power will be a major part of site preparation; a further assumption was that the required manpower will be associated to a large extent with stack sampling, the most complex sampling procedure. Preparation of other sites was assumed to be minimal and/or part of the actual sampling procedure. The installation of special samplers, valves, fittings, etc. is considered beyond the scope of a Level 1 sampling effort.

1.4 ANALYSIS OF SAMPLES

Chapters VII through X specify analysis schemes and procedures that will provide data relatable to all existing EPA standards and those additional data requirements specified above for Level 1 environmental assessment. These schemes identify accepted methods of analysis, anticipated output, and the estimated level of effort required to implement the analysis scheme.

There are seven categories of analysis:

- Organic Analysis – Survey techniques are used to identify compound classes by functional group.
- Inorganic Element Analysis - Based on spark source mass spectroscopy (SSMS) which can perform a general survey of all effluent streams for possible inorganic elements.
- Particulate Morphology – Includes microscopic examination of shape, size distribution, surface features and possible source.
- Water Analysis – Reagent test kits will be used as a supplement for those analyses that are not covered by SSMS or organic analysis.
- Gas Chromatographic Analysis – Consists of on-site analysis of gaseous and/or low boiling organic and inorganic species.
- Opacity – This test will be performed using a simple Ringelmann Chart.
- Bioassay Testing – Includes selected health and ecological testing on all solid and liquid samples, and is designed to measure the environmental and health effects potential of a given source stream in a broad and general manner.

Table 1 shows the recommended sample volumes that must be collected which will result in the listed sensitivities when the recommended analysis method is used. These sensitivities have been selected by PMB-IERL-RTP for both inorganic and organic components so that all species of current interest can be analyzed at levels which at present are the lower limits of environmental concern.

1.5 ACCURACY AND PRECISION OF RESULTS

The accuracy and precision requirements for a Level 1 environmental assessment have been discussed in general terms as being quantitative within a factor of ±2 to 3. In general, most of the sampling and analysis procedures which have been selected for this Level 1 manual are adaptations of standard EPA, ASTM, API, etc., methods which have a accuracy and/or precision factor of ±10-20 percent or better. These requirements, however, have been reduced to fit the economic and philosophical constraints for a Level 1 environmental assessment. In order to determine emissions from a given site to within a factor of ±2 to 3, both the sampling and analytical methods must have a precision which is better than a factor of 2. Thus, if the sampling parameters for a given sample along with the corresponding analyses both had a precision within a factor of 2, then the overall precision can be calculated on the basis of equation (1).

$$\sigma_{total} = \sqrt{\sigma^2_{sampling} + \sigma^2_{analysis}} \qquad \text{eq.(1)}$$

Then, if x were the true value, and the precision limits for both sampling and analysis are within a factor of 2.0, the individual values would range from 0.5X to 2X. Substituting these values into equation (1) gives a range from 0.3X to 3.8X for the precision of the final value which is to be used for the environmental assessment. (For the lower limit $\sigma_{total} = X - \sqrt{0.5X^2} = 0.3X$ and for the upper limit, $\sigma_{total} = X + \sqrt{8X^2} = 3.8X$).

Table 1. Recommended Sample Sizes and Detection Limits

Sample Source		Sample Type	Inorganic	Organic
Stack	$30m^3$ $(1,060ft^3)$	a) Particulate Matter	$0.01\mu g/m^3$	$2\mu g/m^3$
		b) Sorbent Trap, $>C_{12}$ b)	$0.01\mu g/m^3$	$2\mu g/m^3$
		c) Sorbent Trap, G_6-C_{12} c)	—	$10\mu g/m^3$
Gas d)	3 liters	a) General Components	$1\ mg/m^3$ e)	$100\mu g/m^3$ f)
		b) Sulfur Compounds g)	$1\mu g/m^3$	$1\mu g/m^3$
Ambient Air	$480m^3$ a) $(17,000ft^3)$	a) Particulate Matter	$0.01\mu g/m^3$	$30\mu g/m^3$
		b) Sorbent Trap, $>C_{12}$	$0.01\mu g/m^3$	$1\mu g/m^3$
		c) Sorbent Trap, C_6-C_{12}	$0.01\mu g/m^3$	$10\mu g/m^3$
Liquid	10 liters (2.5 gal)	—	$1\mu g/l$ h)	$10\mu g/l$
Solid	1 kg (2.2 lb)	—	1 mg/g	100 ng/g

a) At STP

b) The analysis is terminated for organic material if less than 15 mg ($0.5\ mg/m^3$) of organic components are extracted from the total sample.

c) Assumes that the XAD extract is 2 liters and a 1 µl sample is injected into a G.C. with a flame ionization detector with a 0.1 ng detection limit.

d) A maximum sample size of 10 ml is assigned for all cases.

e) Detection limit is approximately 1 ppm.

f) Detection limit is approximately 0.1 ppm.

g) Detection limit is approximately 1 ppb.

h) Assuming a 0.1 ml sample for SSMS electrode formation and a $10^{-9}g$ instrument sensitivity.

From this explanation, it can be seen that when it is stated that the results are accurate with a factor of three, it means that actual value may lie in a range from 1/3 that value to more than 3 times the value. It should be noted that this is a target accuracy and that some procedures may easily meet these criteria while for others, it may be a slightly optimistic.

CHAPTER II

GAS AND VAPOR SAMPLING METHODOLOGY

2.1 INTRODUCTION (References 1, 3, 4, 7, 8, 9, 10)

This chapter discusses the general methodology for obtaining gaseous samples for analysis. Obtaining a representative sample from a simple gaseous stream can be complicated by stratification from incomplete mixing or by variations in stream components over a period of time. For the purpose of Level 1 assessment, a single grab sample is sufficient, although planning is necessary to ensure that sample acquisition is made at a reasonably representative point (position and time) in the stream or process cycle (see Chapter I).

This chapter discusses the sampling methodologies applicable to the following stream types:

- Process streams, vents, and effluents.
- Fugitive gaseous emissions.

Gaseous process streams refer to contained gases being transported from one area to another. These streams exist under conditions which range from a slightly negative pressure to highly pressurized pipeline systems. Also, the contents of gaseous process streams range from corrosive and toxic process effluents to complex organic mixtures. For the purposes of source assessment, only those internal streams which process influents and effluents to the environment are considered for sample acquisition. Consequently, internal process streams are seldom of concern since they do not constitute influents or effluents in contact with the environment. Exceptions to this rule involve such streams existing prior to control devices or which are held for interim periods prior to discharge, such as holding or surge systems situated in-line prior to flare discharge.

Gaseous process vents are generally found in tank farm areas or in various system operations requiring pressure surge variability.

Gaseous process effluents refer to ducts or flues which are exhausted to the atmosphere and for the purposes of this chapter only the C_1-C_6

and inorganic gaseous effluents from these units are considered. The particulate content along with higher molecular weight hydrocarbons are obtained via the Source Assessment Sampling System, which is discussed in detail in Chapter III.

Fugitive gaseous emissions result from various process leaks such as those found in pumps, valve seals, ducting or process connections and the open transfer or storage of liquid process raw materials, intermediates, and products.

2.2 SAMPLING TEST PREPARATION (References 1, 3, 4)

Complex process operations represent diverse conditions which require careful planning of the sampling activity. This planning should be based on data compiled from actual plant records or from plant personnel familiar with the characteristics of each sampling location. A pre-test Level 1 site survey of process streams and vents for sampling gaseous components involves the following six steps:

1) Obtaining detailed, accurate process flow diagrams. They should be as current as possible and can be updated and supplemented by conversations with plant personnel.

2) Tracing the process flows to establish gaseous outputs. Using the process flow diagrams as a guide, a physical inspection of the system must be conducted to uncover any undocumented output sources or unrecorded equipment modifications.

3) Locating and itemizing process vents.

4) Locating and itemizing stacks and flares.

5) Selecting representative sites. The goal of Level 1 sampling is to uncover any pollution sources and to quantify the emission levels within a factor of ±2 to 3. If, in this sense, toxic materials are discovered, then a full-scale Level 2 analysis will be initiated to quantify the problem. Thus, the selection of representative Level 1 sampling sites should reflect this philosophy of obtaining the type of a sample for analysis rather than typical compliance testing criteria.

6) Recording the physical parameters of the stream in as much detail as possible to facilitate the sampling effort and to aid in post-sampling data reduction. Specific guidelines regarding parameters of interest may be found in Appendix B.

Aside from these general considerations, there are two specific requirements for gas and vapor sampling:

1) All process streams and vent systems recirculated into process streams will require in-line valves for sampling.

2) All vents to the atmosphere require a means of access as well as suitable working space for personnel involved in the sampling process.

2.3 GAS SAMPLING TECHNIQUES (References 11, 12, 13, 14, 15, 16, 17, 18)

As stated in Section 2.1, a single grab sample of each stream in question is sufficient for Level 1 needs. The grab sample may be taken in one of three ways, depending on the pressure of the stream in question. These three grab sample types are high pressure line, grab purge and evacuated grab samplers, and are illustrated in Figures 5, 6 and 7 respectively.

2.3.1 High Pressure Line Grab Samples

The apparatus illustrated in Figure 5 is used when the pressure is high enough in the stream to require a side-split-bleed to provide a sufficient pressure reduction for effective bulb purge. The sampling bulb is the dual valve positive displacement type and is 3 liters in volume. The bulb must be purged with approximately ten volumes of the stream gas before the sample is isolated.

A small glass wool plug is inserted in-line prior to sampling to prevent the influx of particulate matter into the bulb during the purge and sample collection periods.

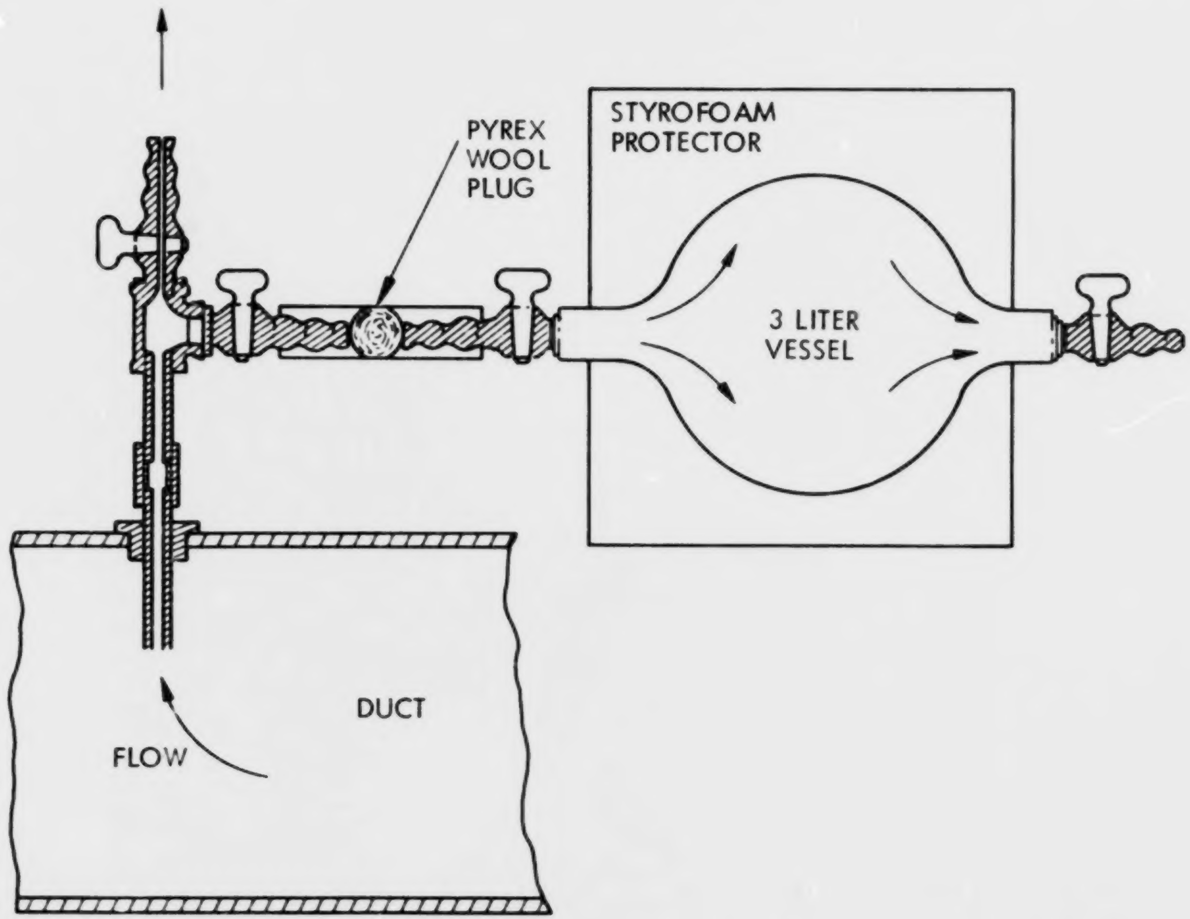


Figure 5. High Pressure Line Grab Purge Sampling Apparatus

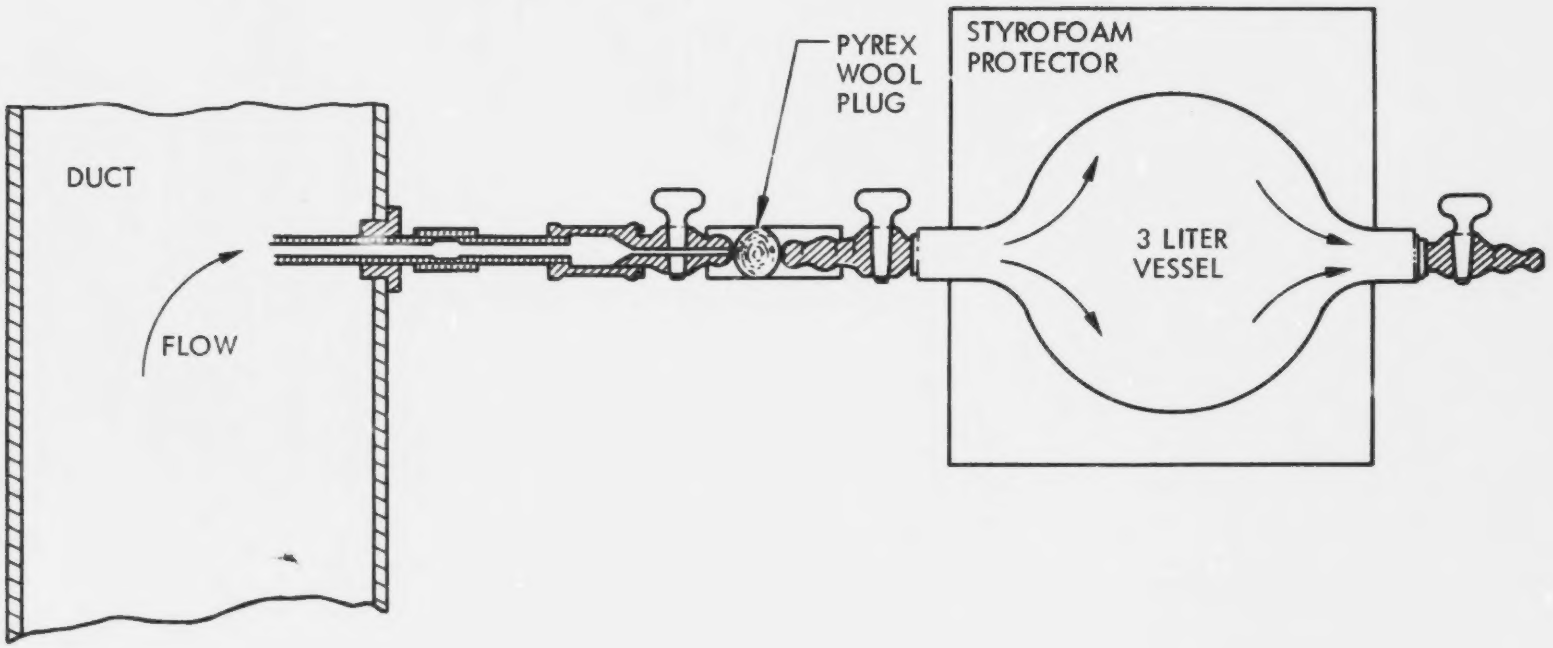


Figure 6. Low Pressure Grab Purge Sampling Apparatus (for Less Than 2 Atmospheres Pressure)

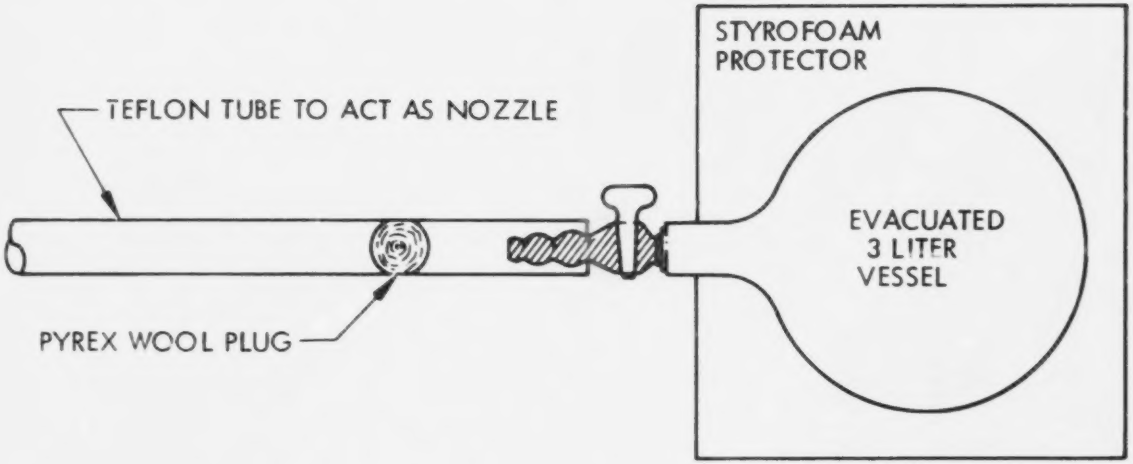


Figure 7. Evacuated Grab Sampling Apparatus (for Subatmospheric Pressures)

2.3.2 Slight Positive Pressure Grab Purge Sampling

The positive displacement dual valve glass sampling bulb described above may also be used in ducts, pipes or vent systems where line pressure is slight. Since the pressure is slight, however, a side-bleed is not required for pressure reduction. Figure 6 shows the apparatus configuration for this sampling method. A small glass wool plug is inserted in-line before sampling is begun, and approximately ten volumes of sample gas must be purged through the bulb prior to isolation of the sample.

2.3.3 Negative Pressure Evacuated Bulb Sampling

Figure 7 illustrates the sampling bulb used for sampling negative pressure systems or open effluent lines such as vent systems or point fugitive emissions (the latter are discussed in Chapter IV).

The bulb is also 3 liters in volume; however, it is the single valve evacuated type rather than the dual valve positive displacement type. The number of bulbs required for a given sampling effort will be known as a result of the pre-test site survey (Section 2.2). The bulbs are then evacuated in the field using a small vacuum pump from the mobile van or trailer. The evacuated bulbs are then taken to their respective sites for sample acquisition.

The entrance nozzle of the bulb must be fashioned so that a piece of tubing can be attached. The tubing acts as a probe to be inserted into either the duct or vent and should be made from 1/4 inch OD Teflon tubing 12 inches in length.

The tube attached to the evacuated bulb is inserted into the vent or negative pressure duct and the sample is withdrawn.

2.3.4 General Considerations

For safety reasons, all of the above described sampling bulbs must be encased in a protective jacket of styrofoam.

Cleaning of the containers is especially important in order to prevent contamination of samples. New glass containers should be conditioned prior to use by allowing them to stand full of distilled water for several days. This conditioning process may be accelerated by rinsing the container with dilute hydrochloric acid followed by distilled water.

After use, containers should be thoroughly cleaned. A 2:1 mix of Alconox or abrasive cleaner and water may be used followed by a tap water rinse. The container is then rinsed with a 1:1 mixture of H_2SO_4 and HNO_3, followed by a tap water rinse of the acid, followed by a final flushing with three volumes of high purity water.

Sampling bulbs cleaned in this way may then be dried, filled with nitrogen and stored until ready for use.

2.4 SAMPLING PROCEDURES

This section briefly describes the problems and considerations involved in sampling process streams, flues and ducts, and vents.

2.4.1 Process Streams, Flues and Ducts

A process stream may require any of the three previously described grab sample types depending on the nature of the stream. A stream under elevated positive pressure will require the apparatus described in Section 2.3.1. Streams under only slight positive pressures and streams under negative pressures will require the apparatus described in Sections 2.3.2 and 2.3.3 respectively.

Whatever sample type the process conditions require, the primary issue involves the careful planning needed for the selection of the most representative sampling point. Frequently, pipeline, duct and vent systems consist of composite streams wherein the main or primary stream is joined in one or more places by secondary streams. When this is the case, a sampling point must be chosen far enough downstream of the joint to ensure component homogeneity. An optimum choice for sample withdrawal in gaseous systems is at a point downstream from a bend in the pipe or duct, since a bend induces turbulence and therefore homogeneity.

In-line valves or sampling ports must also be assessed for their compatability with available apparatus. For example, the process port or valve entrance will in many cases be larger than the bulb entrance. To solve this problem, a series of one-hole stoppers of various size increments may be used to fit over the bulb nozzle entrance.

For the high pressure (Figure 5) and low pressure (Figure 6) sample collection, all sample containers must be purged with approximately ten volumes of the sample gas prior to collection of the sample (this should take approximately 2 minutes). For the subatmospheric pressure (Figure 7) sample collection, the sample should be collected by slowly cracking the valve and letting the sample bleed in (approximately 30 seconds).

2.4.2 Vents

Vent systems generally consist of relief tubes or exit ducts regulated by in-line pressure release valves. Vents are found in holding tanks and storage tanks and are usually discharged into the air when the tank pressure exceeds the pressure setting of the in-line valve. The velocity of the gases being emitted from vent systems, as well as the time duration of the vent cycle, is directly proportional to:

1) The diameter of the vent tube,
2) The headspace volume of the system being vented, and
3) The pressure setting of the in-line relief valve.

Units or tanks with pressure vent releases to ambient air are sampled with a 3-liter evacuated bomb (Figure 7). The important considerations in obtaining vent gas samples are:

- The sample must be taken while the vent cycle is in progress. (Cycle periods for individual processes should be known as a result of the pre-test survey).
- The entrance nozzle of the bomb should be situated so that a representative sample of the vent effluent is obtained without contamination by ambient air.

2.5 SAMPLE HANDLING (References 3, 14, 15)

All gas samples described in this chapter will be analyzed by gas chromatography using procedures described in Chapters VII and VIII. Because many streams contain components which will interact with one another, it is important that the sample be delivered to the mobile unit as soon as possible to avoid significant alteration.

Glass sampling bulbs must be encased in styrofoam protectors to avoid breakage and possible injury to members of the sampling team.

CHAPTER III

GASEOUS STREAMS CONTAINING PARTICULATE MATTER

3.1 INTRODUCTION

Stationary source particulate matter sampling and analysis have been restricted to streams of high mass loading because the sampling flowrates of the sampling equipment have not been high enough to collect an adequate amount of material in a reasonable length of time (Ref. 3, 6, 19). In addition, health effects data indicate that an adequate assessment of the collected particulate matter requires size fractionation into at least four size fractions (Ref. 6, 20). Also, provision must be made for the collection of volatile trace elements and organic species. For all of these reasons, the EPA (IERL-RTP) has developed and specified the use of the Source Assessment Sampling System* (SASS) train (Figures 8, 9 and 10) for the collection of particulate and volatile matter in addition to the gaseous samples discussed in Chapter II.

The sampling train consists of a stainless steel probe which enters an oven module containing 3 cyclones and a filter. Size fractionation is accomplished in the series cyclone portion of the SASS train, which incorporates the cyclones in series to provide large quantities of particulate matter size-classified into three ranges: a) >10 μm, b) 3 μm to 10 μm, and c) 1 μm to 3 μm. Together with a standard 142 mm filter, a fourth cut, <1 μm is obtained. Volatile organic material is collected in a XAD-2 sorbent trap. The XAD-2 trap is an integral part of the gas treatment system which follows the oven containing the cyclone system (see Figure 8). The gas treatment system is composed of four primary components: the gas conditioner, the XAD-2 adsorbent trap, the aqueous condensate collector, and a temperature controller. The XAD-2 sorbent is a porous polymer resin with the capability of adsorbing a broad range of organic species. Some trapping of volatile inorganic species is also anticipated as a result of simple impaction. Volatile inorganic elements are collected in a series of impingers. The pumping capacity is supplied by a 10-cfm high volume vacuum

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*Manufactured by Aerotherm Corporation, 485 Clyde Avenue, Mountain View, Ca., 94042, Tele. (415) 964-3200.

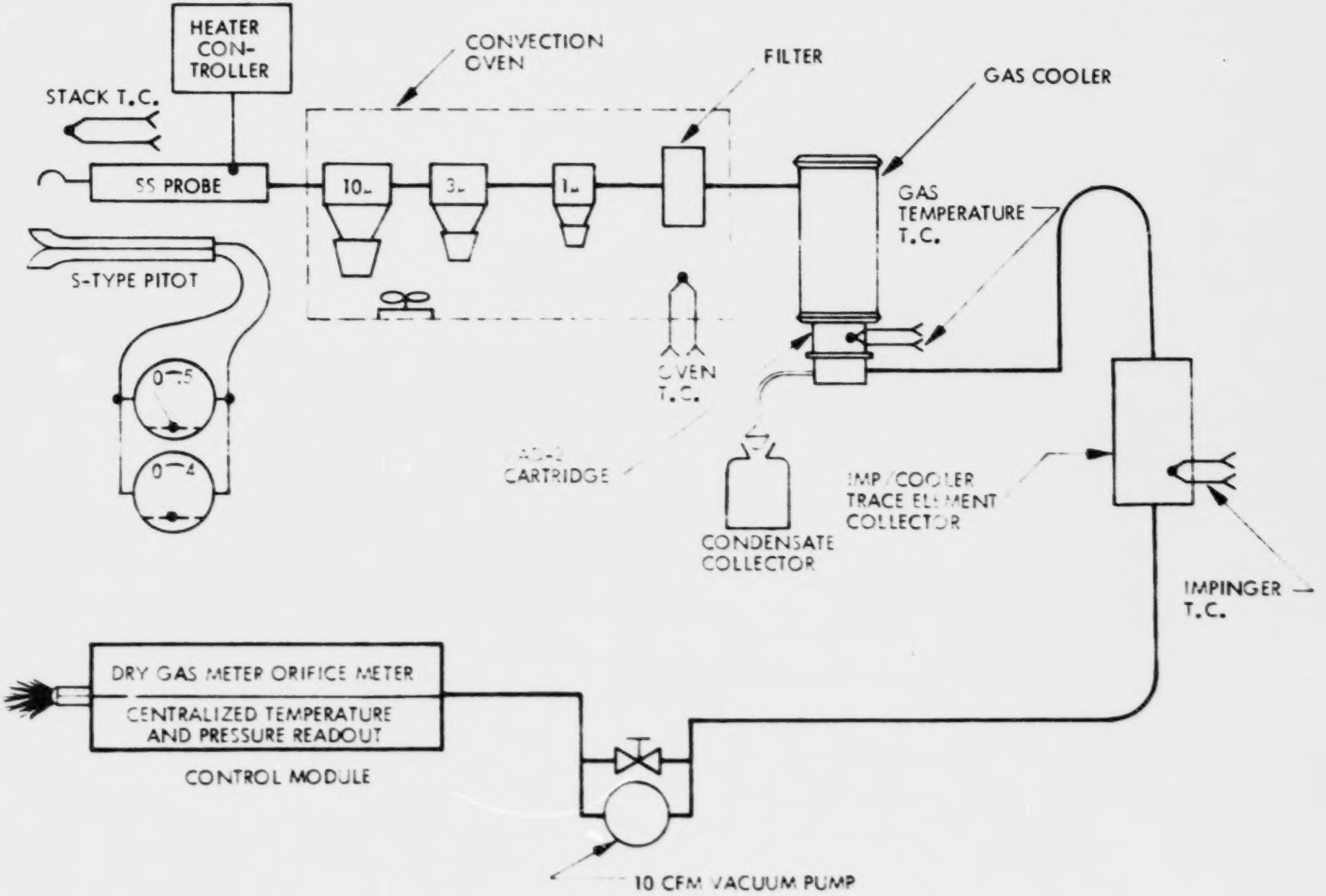

Figure 8. Source Assessment Sampling Schematic

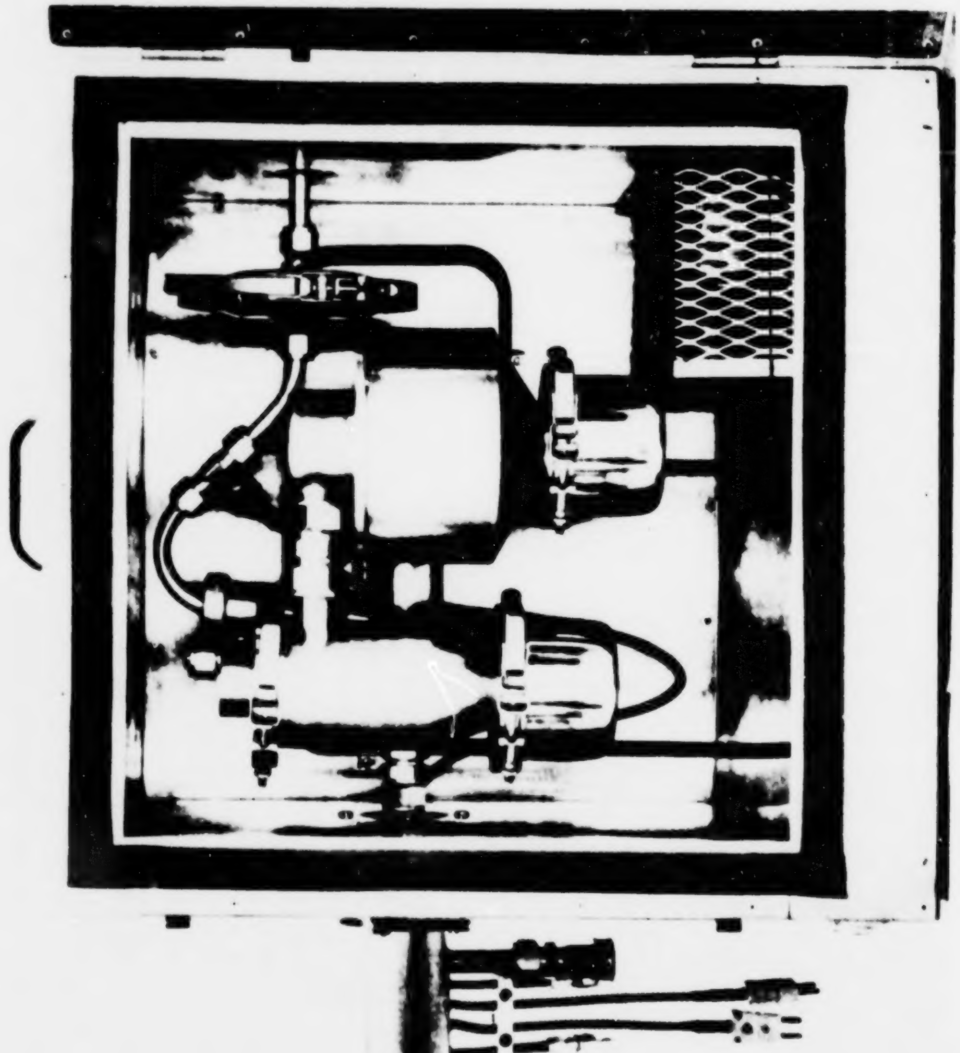

Figure 9. Cyclones and Water Cooled Probe

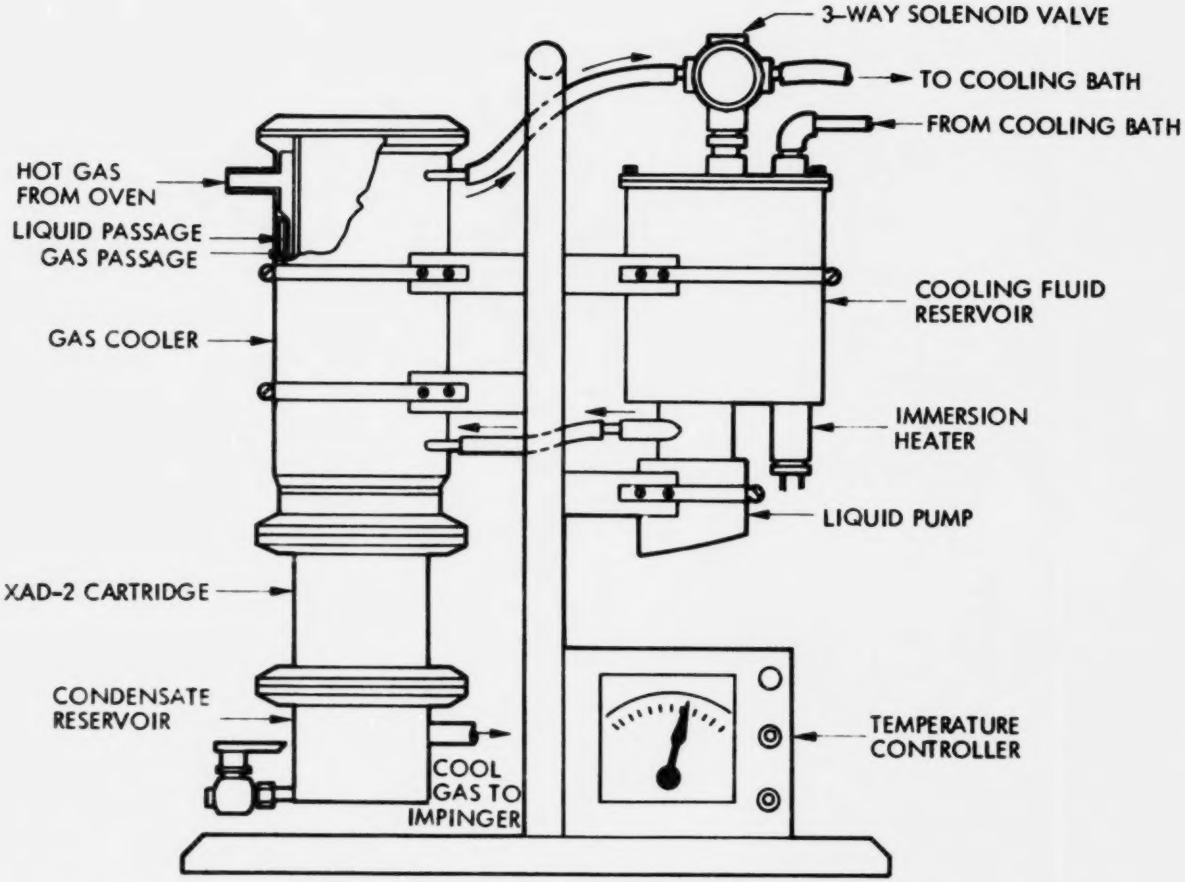

Figure 10. XAD-2 Sorbent Trap Module

pump, while required pressure, temperature, power and flow conditions are obtained from a main controller.

A schematic for flue gas sampling and analysis, which forms the basis for this chapter, is shown in Figure 11. Details of the sample handling and transfer procedures are presented in Section 3.5.

Knowledge of the size distribution of particles emitted from given industrial or energy sources is important to considerations of engineering, environmental and health effects. In the first instance, design and/or evaluation of particulate matter control devices rely upon these data. Secondly, it may be predicted that the large particulate matter fraction will deposit in close proximity to the source, whereas the fine particulate matter which is more difficult to control, will be carried airborne for long distances. These minute particles can often affect weather and visibility and may possibly modify the heat balance of the earth.

3.2 PARTICULATE MATTER SAMPLING METHODOLOGY (References 4, 15, 21, 22, 23)

In normal research and compliance testing, great care is taken to ensure that isokinetic conditions are maintained and that a proper traverse is performed. A Level 1 sample is acquired at the point of average velocity which is determined by a velocity traverse. The sample is withdrawn at a constant flow rate using a nozzle which is specifically selected for isokinetic conditions when the test is initiated. For the accuracy requirements of Level 1, this flowrate is allowed a slippage of from -30 percent to +50 percent of the specified isokinetic rate. Conditions existing outside of the above specified margin must result in SASS train shutdown for an inspection of the problem. The cause of the deviation from isokinetic conditions frequently may be traced to cyclic variations in grain loadings or simply to a continuous high grain loading density, as well as an increase/decrease in gas velocity, or the inability of the pump to pull the volume required to meet particulate matter collection requirements.

Two possible situations occuring within the SASS train will manifest pressure variations outside of the acceptable margin. They are:

1) Clogging of the probe nozzle, and
2) Clogging of the backup filter.

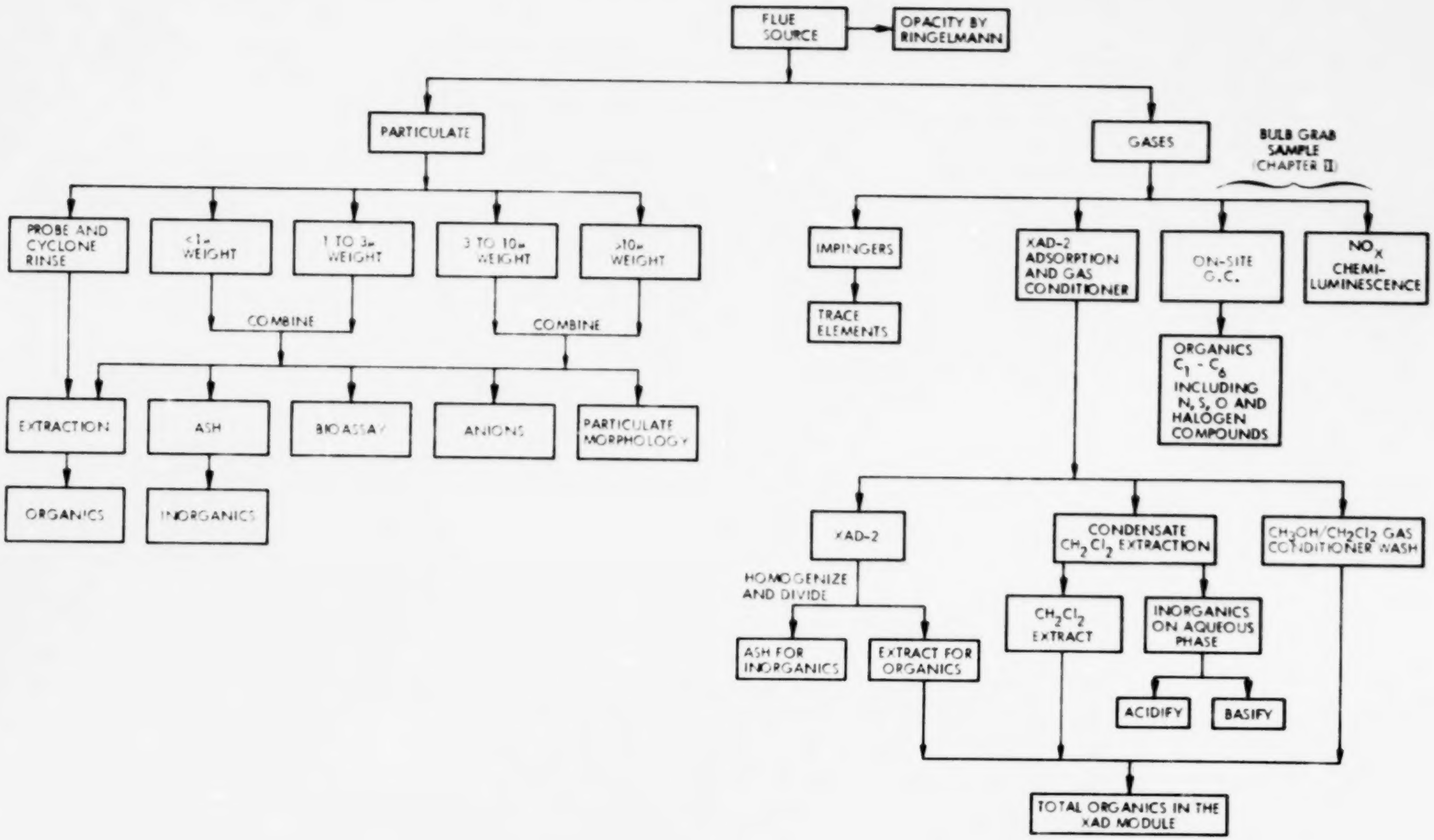

Figure 11. Flue Gas Sampling Flow Diagram

The only possible solution in both cases requires SASS train shutdown and concomitant probe nozzle cleaning or filter replacement.

3.3 PREPARING FOR SAMPLE COLLECTION

3.3.1 Pre-Site Survey

After performing the general site survey and obtaining the necessary process data as described in Chapter I, the survey personnel should select the appropriate sampling site with the following criteria in mind:

- When possible, each sampling point should provide a sample which represents as closely as possible the chemical composition and mass emission rate of the effluent stream. (This is a desirable but not a strict requirement of Level 1 sampling as described in Section 1.3 and 3.2).
- The sampling site must have a reasonably favorable working environment. The survey personnel will consider the temperature and noise level in the sampling areas, whether protection from rain or strong winds exists, and whether safe scaffolding, ladders, pulleys, etc., are present.
- Having located the appropriate sampling location, the physical characteristics of the stream (temperature, flow, grain density, etc.) should be determined from run engineers.

It is intended that the results of the pre-test site survey be sufficiently detailed, so that the field test problems of sampling the correct flue gas stream at the proper sampling location and of using the appropriate methodology will be completely defined prior to arrival of the field test team at the source site. These data should be recorded in the form of a pre-test survey report.

3.3.2 Personnel Requirements

The personnel requirements are related to the magnitude of the sampling task; however, certain general correlations can be made. These correlations can be scaled in a reasonably linear fashion and then applied to the sampling task at hand in order to tailor manpower and time requirements to fit the task (Ref. 1, 6, 24).

The acquisition of a Level 1 sample using a SASS train generally requires two and in some cases, three persons for equipment assembly and disassembly. After assembly the train requires from one to one and one-half persons for operation. The remaining manpower is then available for other on-site efforts.

Each SASS train run will consist of approximately a five-hour period (specific sample acquisition criteria are described in Section 3.4). The number of required personnel for this function will not increase regardless of the number of sample sites, provided that a sufficient time allotment exists within the sampling task to allow for consecutive sampling.

Manpower projections can then be determined by considering the number of SASS particulate matter samples required to characterize the site in question, the time required for the acquisition of each sample (determined as a function of analytical objectives), and the number of personnel and/or samplers available for the task.

3.3.3 Equipment Preparation for Sample Collection

The following sections discuss the equipment preparation required for the SASS train, including cleaning procedures of the train components and sample containers, and apparatus checkout. The SASS train schematic and other parts of the train are shown in Figures 8, 9 and 10.

3.3.3.1 Precleaning Procedures for the SASS Train and Sample Containers (References 3, 4, 6, 25, 45)

The SASS train is the most complex sampling unit discussed in this manual, and an overall generalized cleaning procedure cannot be established. Two primary cleaning methodologies are required. The first methodology, described in this section, concerns the technique involved in producing biologically inert surfaces throughout the SASS train. The second methodology, described in Section 3.5 (Sample Handling and Shipment), presents the techniques required for cleaning or removing sample from various parts of the train after the run.

The first stage in preparing the sampling train and sample containers for sample collection is prepassivation with a nitric acid solution. All surfaces in the sampling train which come in contact with sample, as well as all sample containers and containers for the impingers, should be prepassivated by a one-hour standing contact with 1:1 (v/v) aqueous nitric acid.

Two separate approaches are used for subsequent cleanings: one for SASS train components and organic sample receptacles; and the other for bottles holding impinger solutions. The first group is cleaned in three successive stages using a different solvent in each stage. The solvents used are distilled water, isopropyl alcohol and methylene chloride, in the order listed. This procedure removes all extraneous particulate matter and produces a clean, dry surface. As each part is treated with the final solvent (methylene chloride), it is purged dry in a filtered stream of air or dry nitrogen and inspected throughly for any sign of contaminating residue, scale, rust, etc. A contaminated train component may not be used in a sampling run. All equipment treated in the above fashion must be placed in a clean area to await the next test. Disassembled components of the sampling train which trap particulate matter are to be draped with clean-room grade nylon until ready for use.

The bottles holding the impinger solutions are cleaned in two successive stages, involving distilled water, followed by isopropyl alcohol.

The field area in which these cleaning operations are performed must be as clean as possible under existing field conditions. An enclosed space is required in which reasonable precaution has been taken to remove spurious dust, dirt or particulate contaminants. Reasonable precaution is intended to mean that the area has been swept clean, doors or significant draft inducing sources have been closed and clearroom grade nylon has been spread over the work bench area.

3.3.3.2 Apparatus Checkout

The following tasks should be performed in the home base laboratory prior to field arrival:

1) Gather together all components required for complete system assembly.
2) Clean components in accordance to the above described procedure.
3) Leak check the entire system.

Besides the cleaning procedures, leak checking the train prior to field use is one of the most important pre-test tasks to be performed. This simple procedure can save hours of sampling time in the field. The leak checking procedure involves sealing the probe tip, turning on the pumping system, and observing flow meter gauges for the existence of any appreciable flow. The allowable leak rate for the SASS train is 0.05 cfm at a pressure of 20 inches of Hg. The instructions accompanying the train will present in detail the steps involved in leak checking the system.

3.4 SERIES CYCLONE SAMPLING PROCEDURE

Assuming that the series cyclone system has been cleaned in accordance with the specification presented in Section 3.3 prior to arrival at the site and that all process characteristics have been determined and recorded as outlined above, a Level 1 sample may be taken as follows (Ref. 6):

1) Assemble sampling apparatus in accordance with the manufacturer's specifications.

2) Warm up those components that require preheating. These are the probe, the oven, and the temperature control fluid in the XAD-2 Module. Under most conditions 15 to 30 minutes are required for preheating. The oven and probe should be maintained at 205°C (400°F). The temperature of the cartridge should be kept at 20°C (68°F).

3) Measure the stack temperature, moisture content, and velocity profile. Determine the position in the stack which corresponds to the average stack velocity.

4) Leak test the system. As mentioned earlier in Section 3.3.3.2, the equipment should be thoroughly leak-checked prior to site arrival. If this has been done properly, the on-site leak test should simply be a precautionary formality to ensure that all fittings are properly tightened.

5) Using the procedures and calibration curves supplied by the manufacturer, compute the appropriate sampler flowrate and the proper nozzle size.

6) Fill the impinger bottles with the reagents specified in Table 2.

7) Install the nozzle on the probe, and then insert the probe into the stack or duct. The nozzle should be in the proper position in the duct, as determined in (3).

8) To initiate the sampling run, turn on the vacuum pump and throttle the intake valve to achieve the flowrate determined in (5). (A 3- to 5-cfm sampling rate should be achieved at the dry test meter.)

9) During the course of the run, periodic checks and adjustment of flowrates and temperatures should be made.

Table 2. SASS Train Impinger System Reagents

IMPINGER	REAGENT	QUANTITY	PURPOSE
#1	6 M H_2O_2	750 ml	Trap reducing gases such as SO_2 to prevent depletion of oxidative capability of trace element collecting impingers 2 and 3.
#2	0.2 M $(NH_4)_2S_2O_8$ +0.02 M $AgNO_3$	750 ml	Collection of volatile trace elements by oxidative dissolution.
#3	0.2 M $(NH_4)_2$ S_2O_8 +0.02 M $AgNO_3$	750 ml	Collection of volatile trace elements by oxidative dissolution.
#4	Drierite (Color Indicating)	750 g	Prevent moisture from reaching pumps.

The quantities of sample needed in order to perform the required analyses are presented in Chapter I (Table 1). Naturally, the knowledge of whether or not these quantities have been acquired during the run cannot be obtained until subsequent gravimetric analyses have been performed. For this reason the PMB has developed a series of sampling guidelines criteria for acquiring the required quantity of sample during each run. These criteria are:

- At least one process cycle and 30 standard m^3 (1060 scf) of the process effluent are to be sampled during each run.
- In the event that the process is not cyclic in nature, the 30 standard m^3 figure must still be satisfied over a period of time conducive to obtaining a sample representative of process conditions. A sampling duration of five hours has satisfied this requirement in the past.

To fulfill the above conditions it may be necessary on several occasions (due to high grain loading conditions) to interrupt the progress of the run to change the filter or nozzle due to clogging problems. This is an acceptable procedure; however, care must be taken to avoid contamination in the process of transfer. A detailed log should be kept to record any relevant conditions pertaining to the change.

3.5 SAMPLE HANDLING AND SHIPMENT (References 3, 4, 22, 25, 26)

The procedures used in transferring acquired sample from various portions of the SASS train are extremely involved. To expedite the explanation of the procedures involved in sample transfer and handling, the subject is discussed in terms of a modular approach. For this reason, the SASS train is considered in terms of the following sections:

1) Nozzle and probe,
2) Cyclone system interconnect tubing,
3) Cyclones,
4) XAD-2 module,
5) Impingers.

At the conclusion of the sampling run, the train is disassembled and transported to the mobile lab unit or prepared work area as follows:

1) Open the cyclone oven to expedite cooling, disconnect the probe and cap off both ends.
2) Disconnect the line joining the cyclone oven to the XAD-2 module at the exit side of the filter and cap off a) the entrance to the 10μ cyclone, b) the filter holder exit, and c) the entrance to the join line which was disconnected from the filter holder exit point.
3) Disconnect the line joining the XAD-2 module to the impinger system at the point where it exits the XAD-2 module. Cap off the exit of the XAD-2 module and the entrance line to the impinger system.
4) Disconnect the line exiting the drierite impinger at the point where it leaves the impinger and cap off the impinger exit. Discard ice and water from the impinger box to facilitate carrying.

The solvent system which has been found to be the most effective for line rinse and final cleanout of adhered sample consists of a 1:1 mixture of methylene chloride (CH_2Cl_2) and methanol (CH_3OH).

Since step-by-step procedural instruction in narrative form would be voluminous, time-consuming to follow, and might be confusing to the reader, each step is presented in the following series of flow diagrams (Figure 12 to Figure 14). It is suggested that these diagrams be placed in an easily visible location near the cleaning area as an aid to the sample transfer activity.

3.6 OPACITY MEASUREMENTS

Opacity of stack effluent gas is a required Level 1 data point for each sampled stack. The method to be used for this evaluation is the Ringelmann technique which involves the simple process of comparing stack effluent opacity to a hand-held grid composed of varying shades of grey from white to black. The technique usually requires a person who has been certified to take the reading; however, for Level 1 purposes, this requirement has been waived.

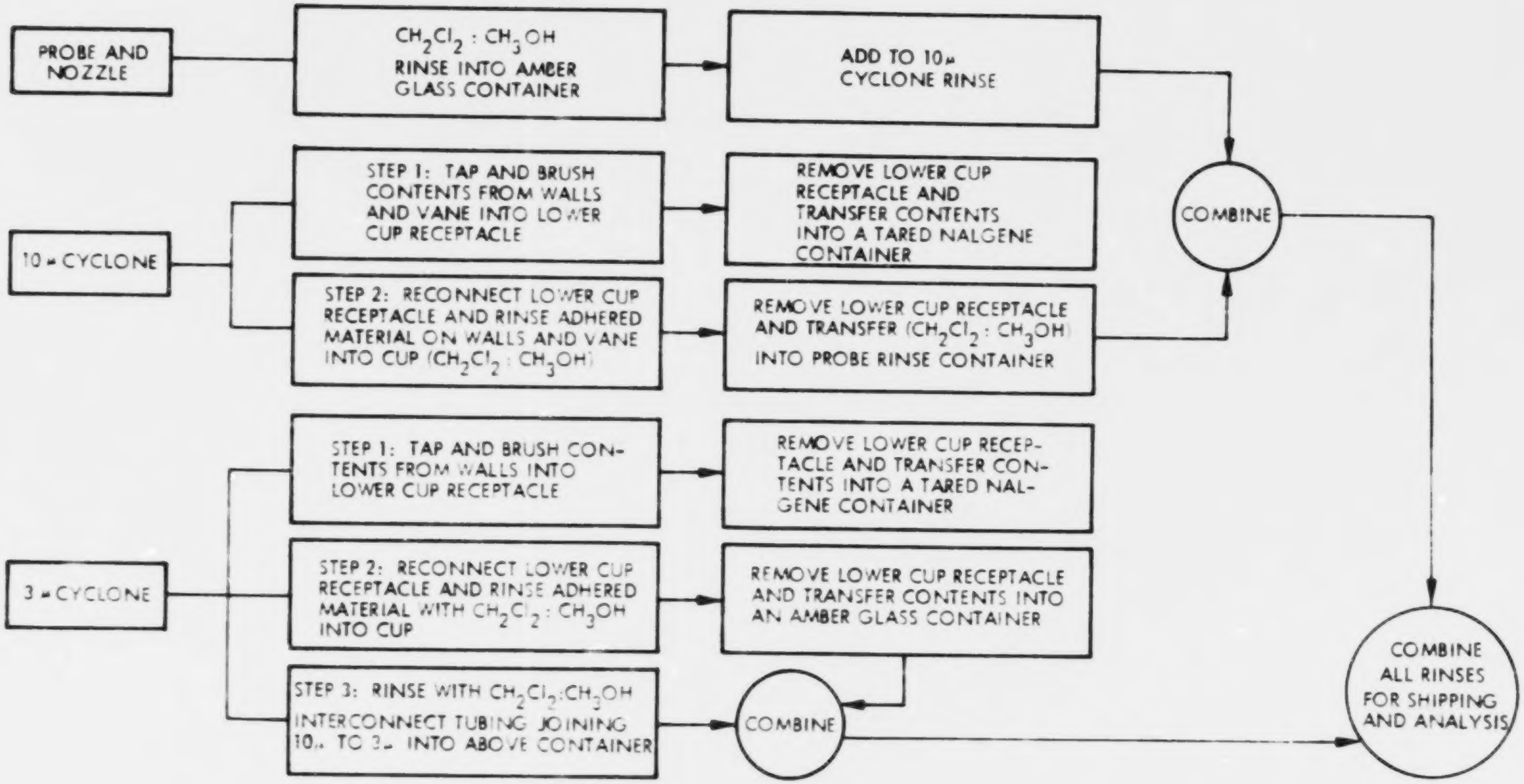
PROBE AND NOZZLE
$CH_2Cl_2 : CH_3OH$ RINSE INTO AMBER GLASS CONTAINER
ADD TO 10μ CYCLONE RINSE
10μ CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS AND VANE INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL ON WALLS AND VANE INTO CUP ($CH_2Cl_2 : CH_3OH$)
REMOVE LOWER CUP RECEPTACLE AND TRANSFER ($CH_2Cl_2 : CH_3OH$) INTO PROBE RINSE CONTAINER
COMBINE
3μ CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL WITH $CH_2Cl_2 : CH_3OH$ INTO CUP
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO AN AMBER GLASS CONTAINER
STEP 3: RINSE WITH $CH_2Cl_2:CH_3OH$ INTERCONNECT TUBING JOINING 10μ TO 3μ INTO ABOVE CONTAINER
COMBINE
COMBINE ALL RINSES FOR SHIPPING AND ANALYSIS

Figure 12. Sample Handling and Transfer-Nozzle, Probe, Cyclones and Filter

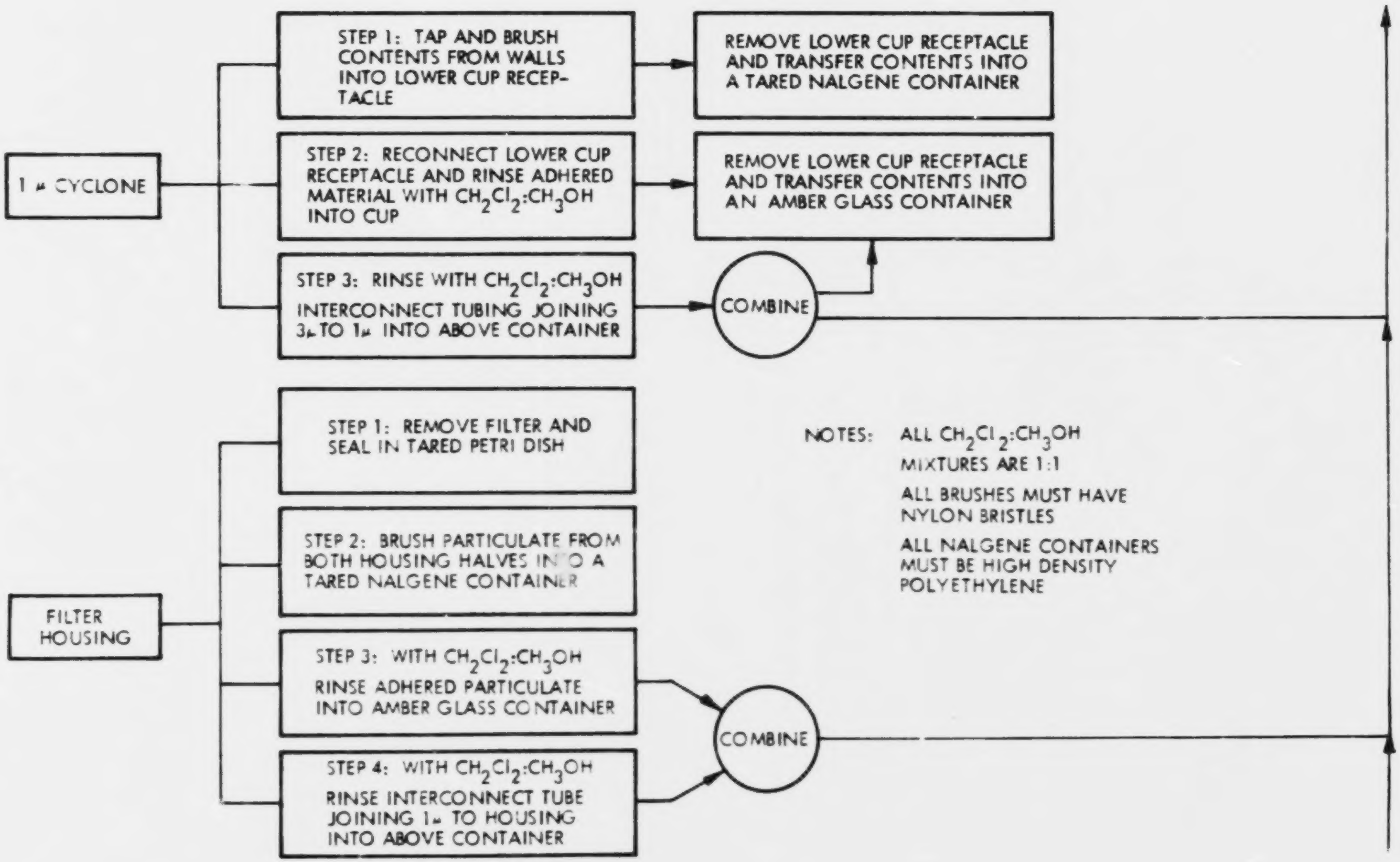
1 µ CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL WITH CH_2Cl_2:CH_3OH INTO CUP
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO AN AMBER GLASS CONTAINER
STEP 3: RINSE WITH CH_2Cl_2:CH_3OH INTERCONNECT TUBING JOINING 3µ TO 1µ INTO ABOVE CONTAINER
COMBINE
FILTER HOUSING
STEP 1: REMOVE FILTER AND SEAL IN TARED PETRI DISH
STEP 2: BRUSH PARTICULATE FROM BOTH HOUSING HALVES INTO A TARED NALGENE CONTAINER
STEP 3: WITH CH_2Cl_2:CH_3OH RINSE ADHERED PARTICULATE INTO AMBER GLASS CONTAINER
STEP 4: WITH CH_2Cl_2:CH_3OH RINSE INTERCONNECT TUBE JOINING 1µ TO HOUSING INTO ABOVE CONTAINER
COMBINE
NOTES: ALL CH_2Cl_2:CH_3OH MIXTURES ARE 1:1
ALL BRUSHES MUST HAVE NYLON BRISTLES
ALL NALGENE CONTAINERS MUST BE HIGH DENSITY POLYETHYLENE

Figure 12. Sample Handling and Transfer-Nozzle, Probe, Cyclones and Filter (Continued)

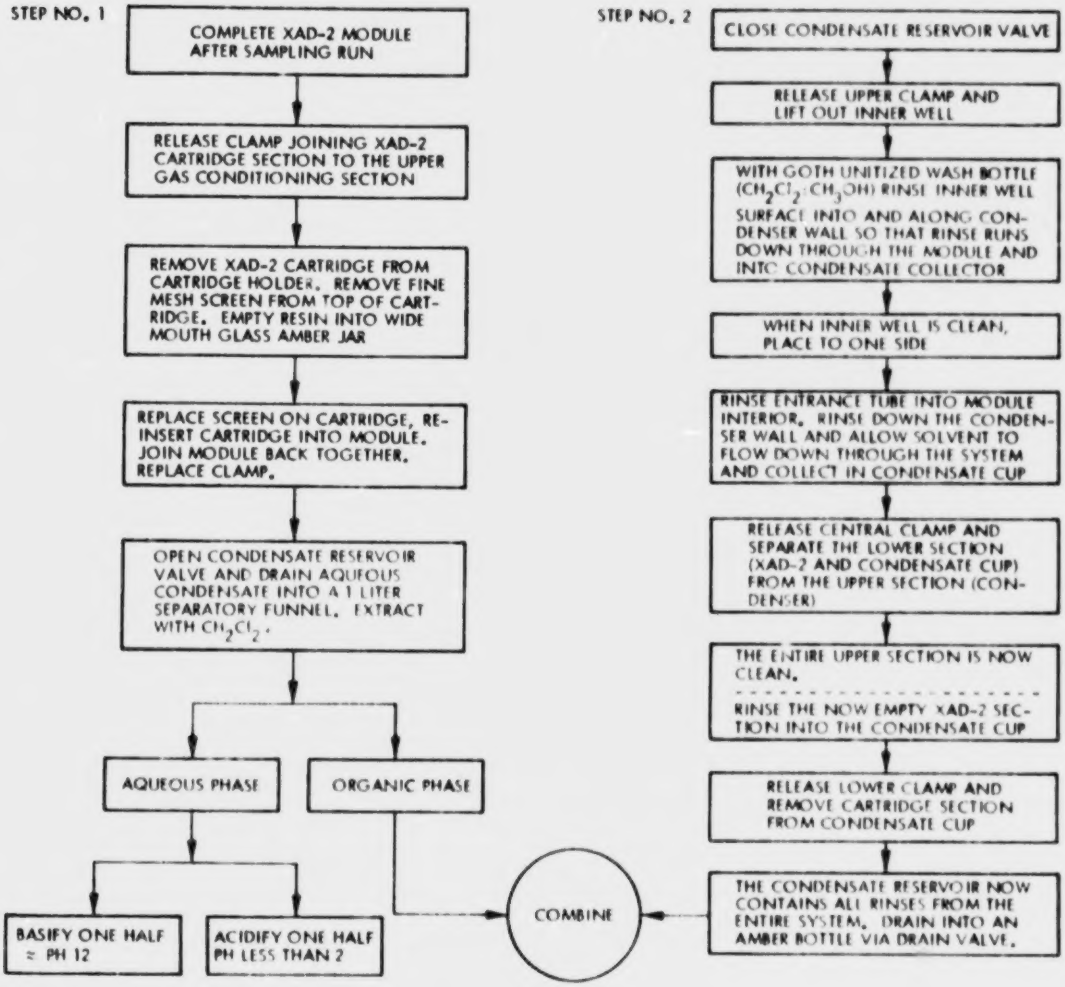
STEP NO. 1
COMPLETE XAD-2 MODULE AFTER SAMPLING RUN
RELEASE CLAMP JOINING XAD-2 CARTRIDGE SECTION TO THE UPPER GAS CONDITIONING SECTION
REMOVE XAD-2 CARTRIDGE FROM CARTRIDGE HOLDER. REMOVE FINE MESH SCREEN FROM TOP OF CARTRIDGE. EMPTY RESIN INTO WIDE MOUTH GLASS AMBER JAR
REPLACE SCREEN ON CARTRIDGE, REINSERT CARTRIDGE INTO MODULE. JOIN MODULE BACK TOGETHER. REPLACE CLAMP.
OPEN CONDENSATE RESERVOIR VALVE AND DRAIN AQUEOUS CONDENSATE INTO A 1 LITER SEPARATORY FUNNEL. EXTRACT WITH CH_2Cl_2.
AQUEOUS PHASE
ORGANIC PHASE
BASIFY ONE HALF ≈ PH 12
ACIDIFY ONE HALF PH LESS THAN 2
COMBINE
STEP NO. 2
CLOSE CONDENSATE RESERVOIR VALVE
RELEASE UPPER CLAMP AND LIFT OUT INNER WELL
WITH GOTH UNITIZED WASH BOTTLE (CH_2Cl_2:CH_3OH) RINSE INNER WELL SURFACE INTO AND ALONG CONDENSER WALL SO THAT RINSE RUNS DOWN THROUGH THE MODULE AND INTO CONDENSATE COLLECTOR
WHEN INNER WELL IS CLEAN, PLACE TO ONE SIDE
RINSE ENTRANCE TUBE INTO MODULE INTERIOR. RINSE DOWN THE CONDENSER WALL AND ALLOW SOLVENT TO FLOW DOWN THROUGH THE SYSTEM AND COLLECT IN CONDENSATE CUP
RELEASE CENTRAL CLAMP AND SEPARATE THE LOWER SECTION (XAD-2 AND CONDENSATE CUP) FROM THE UPPER SECTION (CONDENSER)
THE ENTIRE UPPER SECTION IS NOW CLEAN.
RINSE THE NOW EMPTY XAD-2 SECTION INTO THE CONDENSATE CUP
RELEASE LOWER CLAMP AND REMOVE CARTRIDGE SECTION FROM CONDENSATE CUP
THE CONDENSATE RESERVOIR NOW CONTAINS ALL RINSES FROM THE ENTIRE SYSTEM. DRAIN INTO AN AMBER BOTTLE VIA DRAIN VALVE.

Figure 13. Sample Handling and Transfer - XAD-2 Module

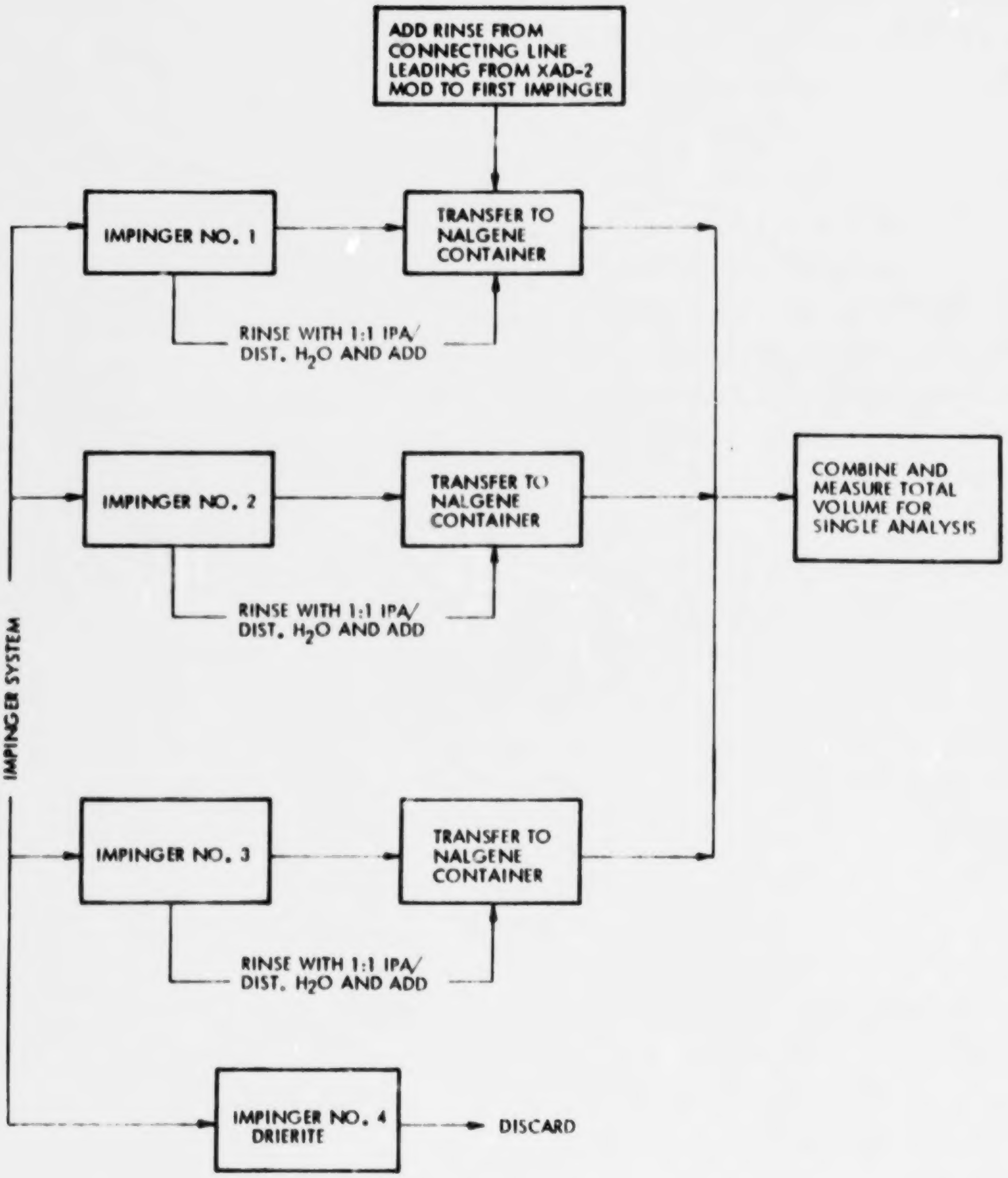
ADD RINSE FROM CONNECTING LINE LEADING FROM XAD-2 MOD TO FIRST IMPINGER
IMPINGER SYSTEM
IMPINGER NO. 1
TRANSFER TO NALGENE CONTAINER
RINSE WITH 1:1 IPA/ DIST. H_2O AND ADD
IMPINGER NO. 2
TRANSFER TO NALGENE CONTAINER
RINSE WITH 1:1 IPA/ DIST. H_2O AND ADD
COMBINE AND MEASURE TOTAL VOLUME FOR SINGLE ANALYSIS
IMPINGER NO. 3
TRANSFER TO NALGENE CONTAINER
RINSE WITH 1:1 IPA/ DIST. H_2O AND ADD
IMPINGER NO. 4 DRIERITE
DISCARD

Figure 14. Sample Handling and Transfer - Impingers

3.7 DATA REDUCTION

Due to the complexity of the SASS train, a broad range of data is acquired as the result of each run. The subject of data reduction is discussed in detail in Chapter I; however, certain aspects specific to SASS train samples are briefly presented here.

After the laboratory analyses have been performed for a specific sample, the data can be applied to the process as a whole. For example, if the laboratory analysis detects 5 ppm Hg in a specific sample, this quantity can be applied to the weight of the total sample that was collected, and can then be further used to calculate the mass emission rate of the entire stream being characterized. In general, the process parameters and conditions determined during the pre-site survey (Section 3.3.1) will serve as the data base to which the analysis results can be applied. For example, data on duct or stack stream velocity and grain-loading density is used to calculate the particulate concentration and size distribution within a stream once the particulate weights from the cyclones and filter are measured. As a result of the data reduction process, general process effluent profiles can be developed for each parameter of interest. The molecular weight or class of organic or inorganic species may be plotted as a function of its location throughout the train. Volatility factors of particulate matter versus gas may be developed. Data points resulting from bioassay analyses may be accumulated.

Data reduction relationships may also be drawn through a comparison of established matrices. For example, it may be noted upon comparison that a relationship exists between the organic matter distribution matrix and the bioassay matrix. Eventually, after several sampling efforts have been conducted for a specific process type (e.g., power plants, coal gasification operations, etc.), a complete characteristic effluent profile for that specific process may be established.

CHAPTER IV
FUGITIVE EMISSIONS SAMPLING

4.1 INTRODUCTION (References 2, 4, 27)

Fugitive emissions are those air and water pollutants generated by any activity at an industrial site which are transmitted from their source directly into the ambient air or receiving surface and ground waters without first passing through a stack, duct, pipe or channel designed to direct or control their flow. The assessment of the effect of a specific fugitive emission on the environment requires determination of the amount of pollutants entering the atmosphere or receiving waters on a weight-or-volume per-unit-time basis.

This chapter presents the basic strategies for the sampling of air- and waterborne fugitive emissions in Level 1 assessment effort. The sampling programs are designed to provide estimates of the major process components emitted as fugitive emissions, within the accuracy limits discussed, in Chapter I.

Fugitive emissions may be generated by almost any industrial operation, including those with specific emission control equipment. Airborne fugitive emissions consisting of particulate matter and gaseous pollutants may be generated by sources enclosed in buildings and transmitted to the atmosphere through structural openings or vents, or generated by sources in open areas and transmitted directly into the atmosphere. In this chapter, any source within a given site generating fugitive emissions which contribute to overall concentrations will be called a specific source. The overall fugitive emissions concentration resulting from the sum total of specific sources will be referred to as the site source. Waterborne fugitive emissions, which consist primarily of suspended and dissolved solids, may be generated by process leaks and spills, runoff from a wide variety of material storage piles, and fallout from emissions initially airborne. They are transmitted to surface waters by runoff and to ground waters by infiltration. Figure 15 summarizes the sampling categories for Level 1 airborne fugitive emissions.

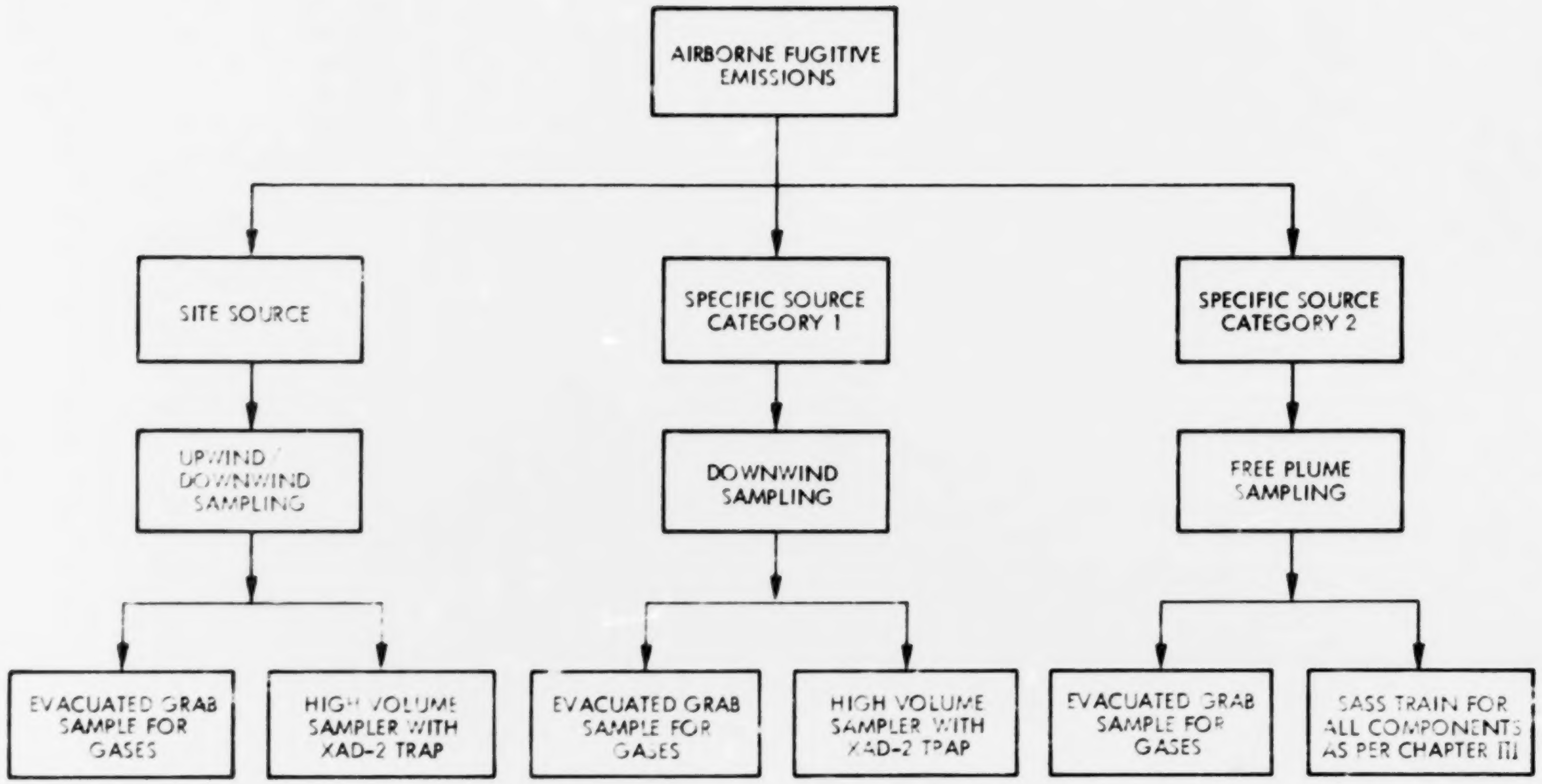
AIRBORNE FUGITIVE EMISSIONS
SITE SOURCE
SPECIFIC SOURCE CATEGORY 1
SPECIFIC SOURCE CATEGORY 2
UPWIND/DOWNWIND SAMPLING
DOWNWIND SAMPLING
FREE PLUME SAMPLING
EVACUATED GRAB SAMPLE FOR GASES
HIGH VOLUME SAMPLER WITH XAD-2 TRAP
EVACUATED GRAB SAMPLE FOR GASES
HIGH VOLUME SAMPLER WITH XAD-2 TRAP
EVACUATED GRAB SAMPLE FOR GASES
SASS TRAIN FOR ALL COMPONENTS AS PER CHAPTER III

Figure 15. Sampling Categories for Level 1 Airborne Fugitive Emissions

Because of the unique nature of fugitive emissions, special techniques applicable to their diffuse nature are used. These techniques include upwind-downwind sampling techniques for site sources, downwind and free plume techniques for specific sources, sampling for waterborne fugitive emissions transported to surface waters, and percolation studies for waterborne fugitives transported to ground waters. The basic aim of this survey effort is not the precise quantitifcation of a given plant's fugitive emissions, but the determination of the fugitive pollution potential so that a detailed Level 2 effort can be planned and executed with a minimum amount of wasted effort.

Unlike other chapters in this manual, the fugitive emissions chapter must be divided into two distinct parts in order to avoid confusion. The first part considers airborne fugitive emissions while the second considers fugitive emissions as they relate to waterborne contaminants. The discussions include technique descriptions, equipment requirements, system design and data reduction and manpower requirement estimates.

4.2 AIRBORNE FUGITIVE EMISSIONS

4.2.1 Preparation for Sample Collection (References 27, 28, 29)

The following sections discuss the preliminary procedures required for sample collection, including the pre-test site survey, the preparation of measurement equipment, and personnel requirements.

4.2.1.1 Pre-test Site Survey

The pre-test site survey for airborne fugitive emissions is extremely site specific and consequently requires many subjective judgments and is treated here in a very general manner. The predominant portion of the survey activity will involve a tour of the overall site in an attempt to identify existing specific sources. If specific sources are found to exist, they must be placed in one or the other of the following two categories:

1) A specific source which generates a highly diffuse cloud over an extensive area, such as coal or ash storage piles.

2) A specific source which generates an emission which might be broadly or generally classified as a plume, such as a coke oven bank.

Naturally, a wide variety of specific sources fall into a nebulous area which could apply to either one of the above two definitions. When this problem exists, the source is to be assigned to the first category.

In addition, a specific source under consideration for fugitive emissions sampling must be significant enough to warrant the effort involved in making the characterization. This is also subjective and a pro or con decision must hinge on the likelihood of the emission's migration beyond the site boundaries. If uncertainty exists concerning specific source significance criteria, disregard the source under the assumption that the site source samples will supply the needed data.

Having identified sampling positions for all significant specific sources within a site, the next step involves locating suitable upwind-downwind locations for the site source samplers. One or more upwind and downwind samplers are required, which depends on the location, size of the site or the homogeneity of the emissions as they exist at the boundary areas.

Clearly, in view of the above criteria, a specific example cannot be developed to consider the diverse contingencies likely to be encountered throughout a variety of sites. However, an understanding of the magnitudes involved is facilitated by considering optimal sampler locations for a "worst case" site. Such a site is considered in the decision example shown in Figure 16 wherein optimum sampler locations are indicated for various specific sources as well as for the overall site. This decision aid is discussed in detail in Section 4.2.3.

4.2.1.2 Measurement Equipment (References 21, 27, 30)

High Volume Sampler. The high volume sampler package identified for Level 1 sampling consists of three primary components:

1) A commercially available, high volume filter device for particulate matter identification,

2) An XAD-2 absorbent trap for C_6 organics, and

3) A 5-cfm pump for the XAD-2 cartridge.

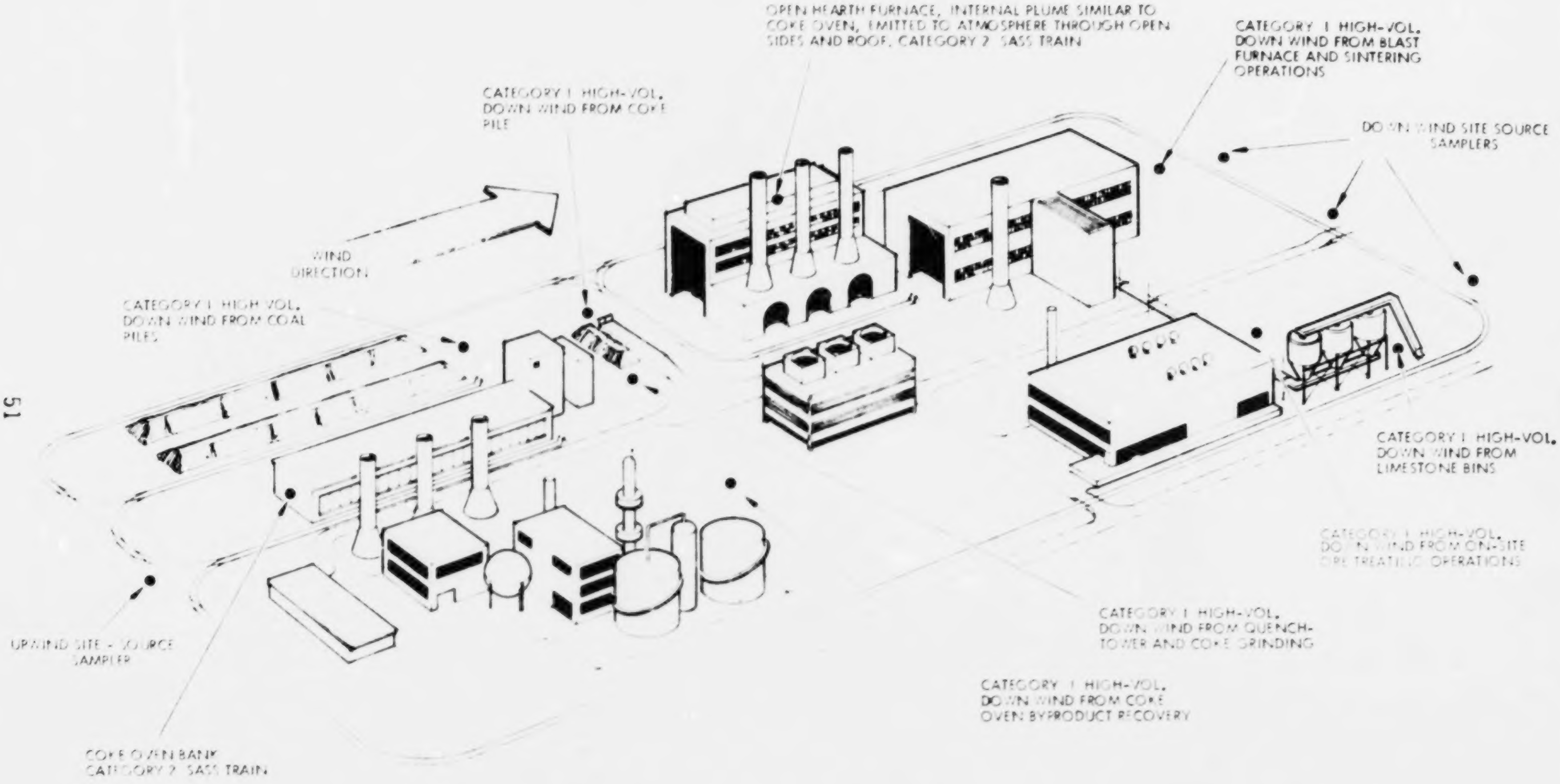
OPEN HEARTH FURNACE, INTERNAL PLUME SIMILAR TO COKE OVEN, EMITTED TO ATMOSPHERE THROUGH OPEN SIDES AND ROOF. CATEGORY 2 SASS TRAIN
CATEGORY 1 HIGH-VOL. DOWN WIND FROM BLAST FURNACE AND SINTERING OPERATIONS
CATEGORY 1 HIGH-VOL. DOWN WIND FROM COKE PILE
DOWN WIND SITE SOURCE SAMPLERS
WIND DIRECTION
CATEGORY 1 HIGH VOL. DOWN WIND FROM COAL PILES
CATEGORY 1 HIGH-VOL. DOWN WIND FROM LIMESTONE BINS
CATEGORY 1 HIGH-VOL. DOWN WIND FROM ON-SITE ORE TREATING OPERATIONS
CATEGORY 1 HIGH-VOL. DOWN WIND FROM QUENCH-TOWER AND COKE GRINDING
UPWIND SITE - SOURCE SAMPLER
CATEGORY 1 HIGH-VOL. DOWN WIND FROM COKE OVEN BYPRODUCT RECOVERY
COKE OVEN BANK CATEGORY 2 SASS TRAIN

Figure 16. Decision Example for "Worst Case" Site

In most common types of high volume filters, a high speed vacuum-cleaner type motor is utilized to draw large volumes of air through a filter to trap the entrained particulate matter on the filter surface. A number of such devices are commercially available and may be utilized interchangeably if the following general specification can be met:

- Flowrate - This should be variable between 0.57m^3/min and 1.7m^3/min (20 to 60 cfm). This variability is needed in order to compensate for differences in particulate density.
- Filter size - 20.3cm x 25.4cm (8"x10") Spectrograde glass fiber filters (Gelman Instrument Co. or equivalent).
- Automatic Flow Control - Most commercial instruments have optional automatic devices to keep a constant flowrate as particulate matter builds up. This type of control is recommended to promote accurate, unattended flow control.
- Construction - Lightweight and durable, capable of all-weather operation in plant environments.
- Cyclic Timer - The sampler should have the capability to sample continuously for a set period of time or intermittently during a sampling period to match the cyclic nature of plant processes.
- Electric Generator - In many cases, a portable electric generator(s) will be required to operate the samplers.

In addition to these requirements, it is recommended that a particulate size fractioning head be added to the high volume sampler. Particle size fractioning heads are available (Anderson 2000 Inc.) which fit directly on high volume samplers. For Level 1 sampling, a single stage head (40 cfm) providing a cutoff at 3.5μ and a back-up filter is recommended.

Grab sampling of gases may be accomplished using 3-liter containers as described in Section 2.3.3.

The XAD-2 adsorbent trap is described as part of the source assessment sampling system (SASS) train in Chapter III. A similar trap (equal in volume but with different end fittings) is connected as an integral part of this system as indicated in Figure 17.

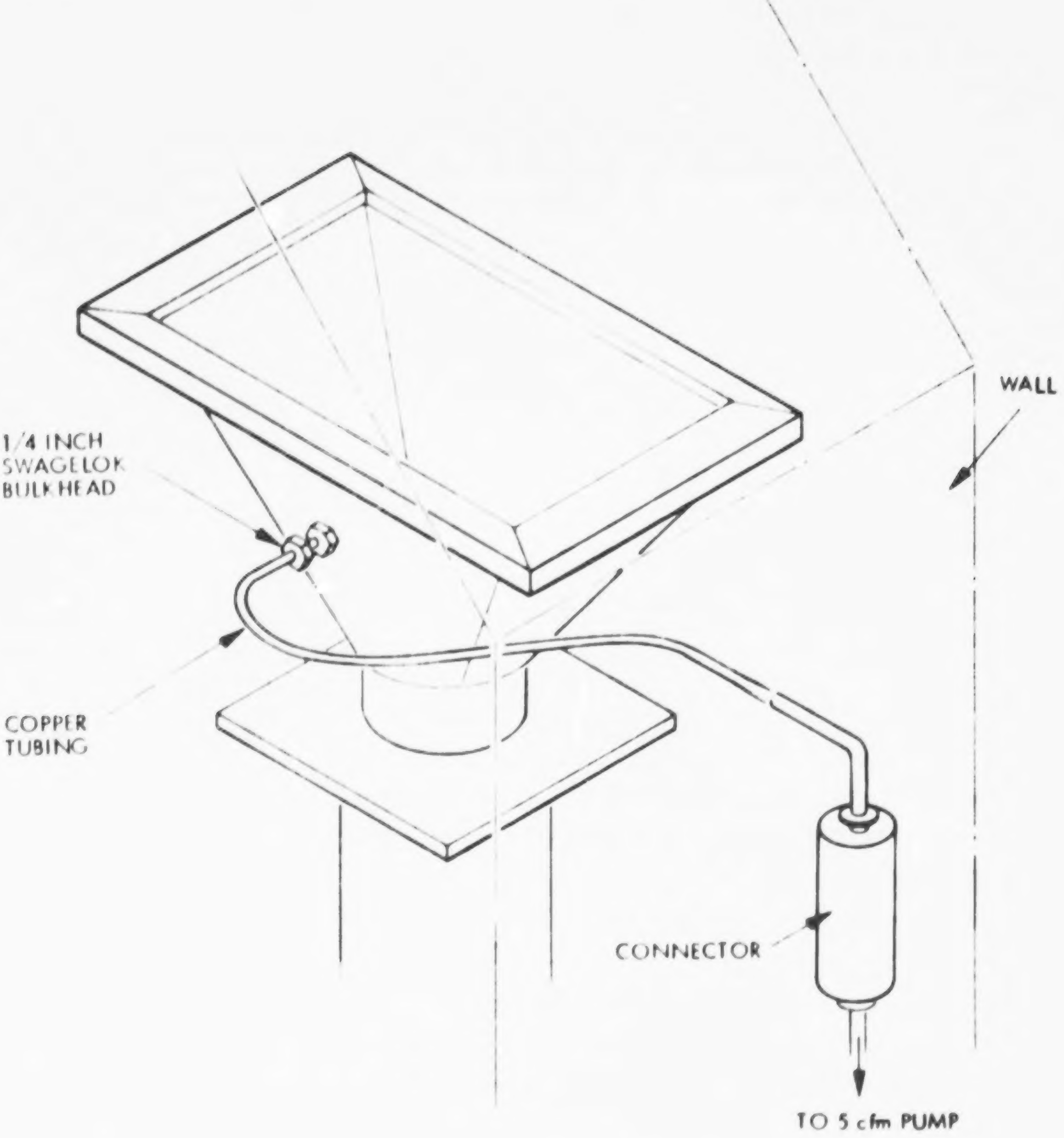

Figure 17. Expanded View of Connections of XAD-2 Cartridge to High Volume Sampler

SASS Train. A detailed description of the SASS train which is to be used to sample Category 2 specific sources which generate plumes is presented in Chapter III. A detailed discussion of the application of the SASS train to fugitive emissions sampling will be presented below in Section 4.3.

4.2.1.3 Personnel Requirements (References 1, 2, 27, 29, 31)

As an outgrowth of the pre-test site survey, the exact number of sampling locations required for the fugitive emissions study may be used as the basis for establishing manpower projections. Two team members are required to set up each high volume sampling station. Assembly and activation will require approximately two hours depending on sampling site accessability. Standard sampler housings as specified in Federal Register, Part 50, Section 5 (Ref. 30) are sufficient for Level 1 purposes; long elevating poles or platforms are not required. After activation, sampler operation is automatic and does not require supervision. Manpower requirements for the hi-vol sampling matrix may then be estimated as a function of the anticipated number of sampler locations.

As indicated in Chapter III, Section 3.3.2, the SASS train requires two and in some cases three persons for assembly and disassembly. One to one and one-half persons are required for operation. These projections apply only to stack or duct sampling conditions where railings, platforms and supportive port openings are available, however. For fugitive emissions sampling, few or none of these conveniences will exist. The probe will in many cases have to be held or at least supported manually; continuous supervision will be required to ensure that the probe is held within the emissions plume. Obtaining the required amount of sample (see Table 1) will often require extended sampling periods. Often, site geometry will require remote equipment setup with lengthy webbed cable probe extensions which in turn will require heat tracing. These and a variety of other factors must be considered (depending on specific site requirements) before manpower estimates for this activity can be established.

A best possible case assembly and disassembly will require from 3 to 4 persons; operation will require no less than two persons. Still, a best possible case setup will require from 5 to 6 hours and the operating period will depend on the density of the plume and the frequency of the cycle (assuming the process is cyclic). The decision to place a specific source in Category 2 for cost effectiveness reasons must not be made lightly. Figure 16 can again be used to clarify the general process magnitudes applicable to specific sampling types.

4.2.2 Sampling Procedures (References 27, 28, 29, 30, 31)

4.2.2.1 High Volume Sampler Applications

The modified high volume sampler, as described in Section 4.2.1.2, will be used in all first category specific sources (see Section 4.2.1.1) and all site source sampling operations.

The number and location of upwind-downwind devices used to collect samples are extremely important to the successful completion of a Level 1 sampling matrix. The design of the system is influenced by such factors as source complexity and size, site geometry and prevailing meteorological conditions. Generally, only one upwind device is required in order to supply background data and one or more downwind samplers are needed depending on the above stated factors. Downwind site-source samplers are to be removed as far as possible from any process operation since the objective in this case involves the collection of a measured portion of a homogeneous cloud as it passes beyond the plant boundary.

First category specific source samples need only be taken on the downwind side of the source. These samples are all taken external to the source and should be placed within the actual cloud if possible. In contrast to the site source samplers which are removed as far as possible from any process operaton, specific source samplers are placed as close as possible to the actual specific source.

Subjective estimates of existing cloud densities may be applied to the curves provided in Figure 18 as a general guideline for time versus flowrate settings.

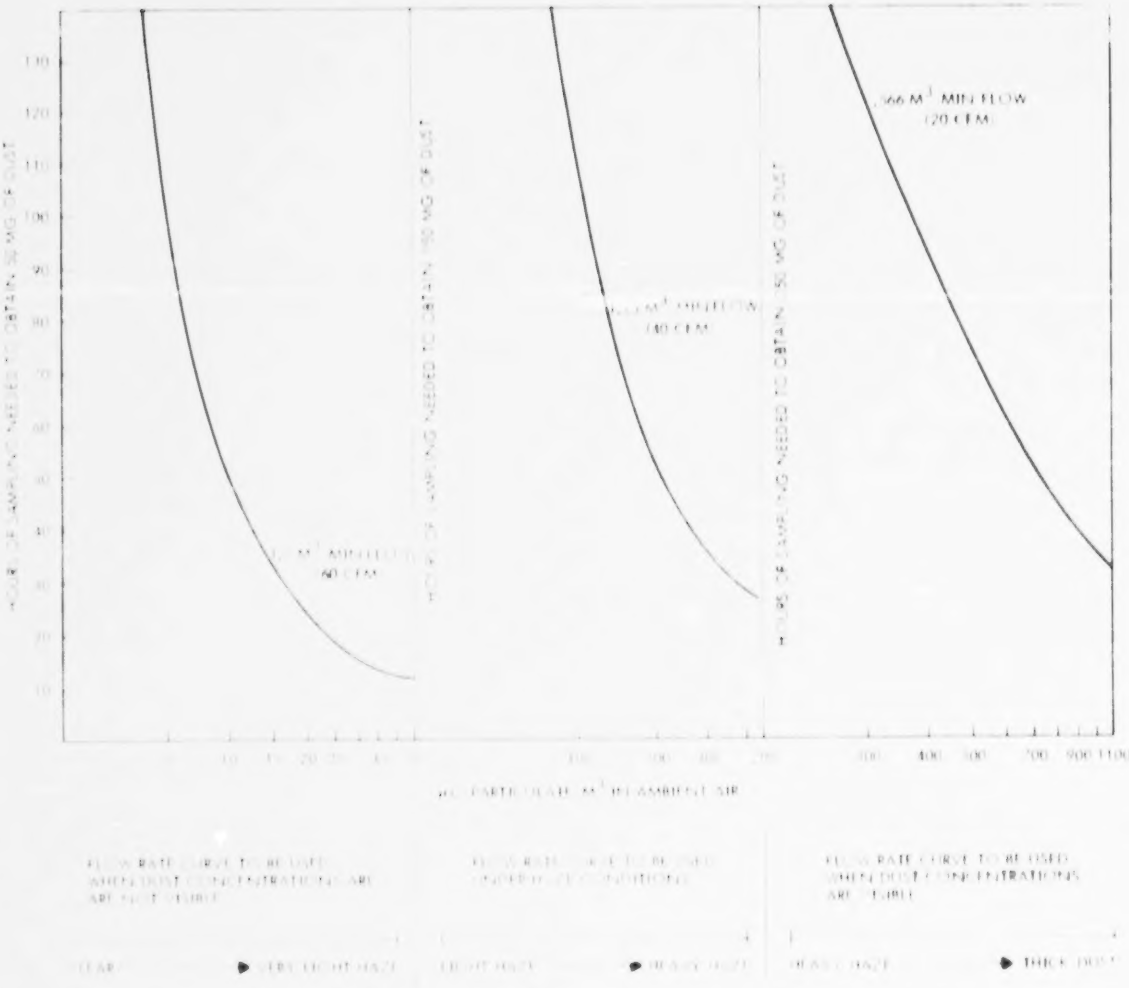

Figure 18. Sampler Flow Rate Settings for Dust

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4.2.2.2 SASS Train Sampler Applications

Fugitive emissions falling into the second specific source category (see Section 4.2.1.1) are sampled with the SASS train. The minimum sample quantities per run, as shown in Table 1, apply here as well.

No two second category specific sources will ever have the same (or even similar) site geometry. Plume characteristics (temperature, area, velocity, density, composition, cyclic frequency, etc.) will also vary markedly depending on process type, size, meteorological conditions and the existence or nonexistence of control devices. Because of these extremely diverse conditons, only generalized procedures may be presented concerning fugitive emissions characterization with the SASS train.

The first consideration involves taking every precaution to ensure the health and safety of personnel directly involved in the sampling task. Personnel assembling the train and especially the person responsible for holding the probe in the plume will be either partially or totally immersed in the escaping gases, and depending on the nature of the effluent varying degrees of protective clothing will be required. Depending on the length of exposure this may require clothing ranging from a simple dust mask to a complete fireproof outfit equipped with self-contained breathing apparatus.

The second consideration involves a choice of the optimum position for sample withdrawal. This position cannot be chosen during the survey effort because specific sources of the second category (and in many cases, in the first category also) are dependent on a number of process and meteorological variables which either may or may not exist on the return trip. The optimum position for sample withdrawal should also be an acceptable location for all train components following the probe. If the above integrated arrangement is not possible, the next best choice involves keeping probe and cyclone oven together while removing the rest of the components to whatever distance the process geometry demands. If the arrangement is such that room for the probe only exists, the entire remainder of the system must be placed in a remote location. In any case, where one component of the train must be isolated from another component, the lines joining the two must be heat-traced to avoid condensation. Assembly and operation of the SASS train is detailed in Chapter III. A fugitive emissions sample is taken with the SASS train by inserting the nozzle into the plume or cloud and pulling at the maximum allowable flowrate using the largest available nozzle. Naturally, the closer the nozzle to the emissions exit point, the denser the plume and the shorter the sample duration.

4.2.2.3 Gas Samples

The acquisition of gas samples for fugitive emissions requires very little elaboration here. All gas samples for Categories 1 and 2, as well as for site source upwind-downwind, will be taken by the evacuated grab sampling technique which is presented in detail in Chapter II.

4.2.3 Decision Aid for Appropriate Category Selections

As previously stated, the sampling matrix for airborne fugitive emission characterization results from the choice of three available options: site source samples, Category 1 specific source samples, and Category 2 specific source samples. The location of sampling positions for the site source case simply involves selecting the proper sites for the upwind and downwind samples. Sampling position for specific sources, which must be classified into Categories 1 or 2, are not as easily identified as the site source. For this reason, a worst-case model is presented (Figure 16) in which a wide variety of specific sources are known to exist. The model, which represents an integrated steel plant is not intended to be viewed as a specific case representation, but provides an example of many of the specific sources found individually in smaller and less complex operations grouped together as an integrated unit.

As indicated in Figure 16, Category 1 is assigned to positions in relatively open areas but which are near specific sources of emissions: downwind from coal and coke piles, and limestone bins; and downwind from blast furnace and sintering operations, ore-treating operations, coke quenching and grinding operations. Category 2 is assigned to positions where plumes are generated, such as coke oven bank, and an open hearth furnace.

4.2.4 Sample Handling and Shipment (References 3, 4, 6, 25)

Quantitative transfer of the samples from the 3.5μ size fractionating head and the filter is necessary in order to determine existing particulate densities. The > 3.5μ catch can be removed from the head by tapping the head and carefully brushing any adhering material into a tared high density Nalgene shipping container. The glass fiber filter must be transferred into a petri dish and sealed without particulate matter loss. During the sampling process, the filter materials have been subjected to conditions which tend to weaken their cohesive properties, so care must be taken to prevent filter fragmentation during the transfer.

After the sample containers have been sealed, the samples may be taken to the mobile van for shipment to the laboratory.

The XAD-2 cartridges are emptied into amber glass jars with Teflon seals and shipped to the laboratory for extraction and analysis. The exact procedures for SASS train sample handling and train clean-up are given in Chapter III.

SASS Train Samples - Lines and containers are rinsed with methanol/methylene chloride and stored in an amber bottle.

Gaseous Samples - All gass bulb samples are taken to the mobile facility for on-site instrumental analysis.

4.2.5 Data Reduction for Airborne Fugitive Emissions (Reference 2, 24, 27)

When the sampling program has been completed and the samples have been analyzed to yield qualitative pollutant concentrations in such terms as micrograms per cubic meter in the ambient air at the individual or combined downwind sampling sites, the measured upwind concentrations are subtracted to yield the concentration provided by the source at each sampler. A library of computer programs to assist in the performance of this assessment is maintained in the User's Network for Applied Models of Air Pollution (UNAMAP) at the Environmental Protection Agency's Research Triangle Computer Center. Additional programs may be obtained through many environmental consultants.

4.3 WATERBORNE FUGITIVE EMISSIONS

4.3.1 Preparation for Sample Collection

The following sections discuss the preliminary procedures required for sample collection, including the pre-test site survey, the measurement techniques required, and personnel requirements.

4.3.1.1 Pre-Test Site Survey (References 32, 33, 34, 35, 36)

Like airborne fugitive emissions, waterborne fugitive emissions are very site specific. In designing a water fugitive emissions survey, the following general strategy should be used:

1) Assess operating procedures to see where waterborne fugitive emissions originate, e.g., material storage piles, overflow from impoundments, runoff from construction, dust from conveyors.

2) Obtain the necessary background information, including topographic data, soil data, geological information, hydrology, climatology and meteorology, surface cover, land use.

3) Locate runoff sampling stations based on the drainage basins identified from a topographic survey.

4.3.1.2 Measurement Techniques (References 32, 33, 34, 35, 37)

A variety of techniques for the measurement of waterborne fugitive emissions is in use today. These techniques include water runoff, receiving body sampling and core sampling. The method of choice for the Level 1 characterization of waterborne fugitive emissions is surface runoff sampling.

This method is utilized for sources that can be identified as contributors to the pollution of water at an industrial site and whose runoff during a rainfall may be isolated from that of other sources. An example of such a source is a storage pile containing materials which will be carried either as suspended or dissolved pollutants by surface runoff to the environment outside plant boundaries.

Topographic data and a site survey are used to locate an array of samplers arranged to collect representative portions of the runoff during a rainfall. The samples are usually located in the ground as close to the source as possible and in natural gullies and channels. Samples are taken at the onset of a rainfall and at intervals during the rainfall and analyzed to determine the change in pollutant concentration as a function of the amount of runoff determined by rain gage measurements. This change in concentration may be used to estimate the amount of polluting material that may be expected to reach the receiving body as a result of any single or an entire season's rainfall.

4.3.1.3 Personnel Requirements

Personnel requirements for placing the sampling plugs are in most cases minimal. One team member will be able to complete the activity in a relatively short period of time. The actual time required is dependent on the proposed area of the monitored zone and the ease of accessibility to that area.

4.3.2 Sampling Procedures (References 38, 39, 40, 41)

For the sampling of contaminated runoff, such as a material storage pile, plug collectors similar to that shown in Figure 19 are used.* The plugs are driven into the ground at selected locations where runoff will occur, such as at the base of the material pile, and in material gullies and channels.

During a rainstorm or snow-melt, the collectors are changed at appropriate intervals depending upon runoff intensity. The collector contents are measured and analyzed for pollutants as discussed in Chapters VII and VIII. An estimate of the runoff flow is made from total rainfall data and soil permeability in the test area.

4.3.3 Decision Aid

The area designated for characterization must be carefully studied by those individuals responsible for this activity. Key areas to identify are:

- Coal piles
- Waste piles
- Drainage trenches for plant system runoff, and
- Possible overflow areas from holding ponds.

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*Plugs are designed and built by Kahl Scientific Instrument Corp., P.O. Box 1166, El Cajon, California 92022

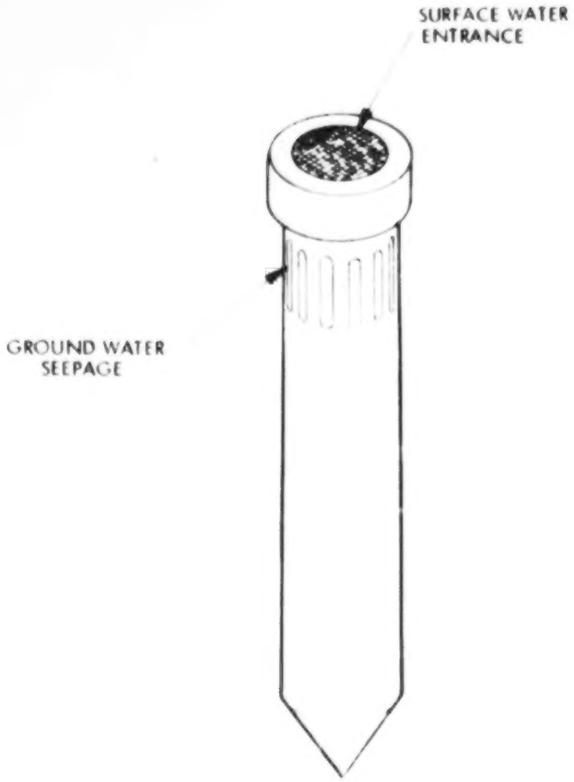


Figure 19. Plug Collector for Fugitive Water Samples

Good areas for collector placement are:

- Areas of lowest elevation where sample throughflow is evident.
- Drainage ditches or channels, and
- Any areas between the complex under consideration and a receiving body of water.

Maximum precaution must be taken to ensure proper collector placement so that data obtained may be related to the proper source. Water runoff samples are similar to airborne fugitive emissions in that both specific source and site source samples are obtainable. Collectors placed for general plant runoff are analagous to site source upwind/downwind samples, and collectors placed for specific problem areas are analagous to specific source downwind samples.

4.3.4 Sample Handling and Shipment

Runoff samples from specific sources are to be combined in order to perform a single analysis to characterize a potential problem area. This minimizes the error which might otherwise result from sample analysis on a unit basis.

After combining the samples obtained from a specific source together into one unit, the resulting single sample is subjected to the same separation scheme indicated in Figure 23 (Chapter V). The only digressions from the Figure 23 flow plan are:

1) BOD and COD analysis are not performed, and
2) A 10-liter volume is not required.

The stabilization procedure applicable to the resulting phases must concur with the directives indicated in Table 3.

4.3.5 Data Reduction for Waterborne Fugitive Emissions (References 33, 37, 39, 41)

The samples obtained from the runoff plug samplers are analyzed to provide pollutant concentrations as a function of time from the start of the sampling period rainfall. Plotted against the measured rainfall rate, they will provide an estimate of the amount of pollutant that can be expected to be received for that period, and, by extrapolation, the amount of pollutant that can reach the receiving body for any given number of rainfalls. Historical meteorological data on the average or maximum rainfall frequency and rate can then provide an assessment of the site or source contribution for a seasonal period.

Figure 20 is a block diagram summary of the waterborne fugitive emissions Level 1 assessment programs described in this section.

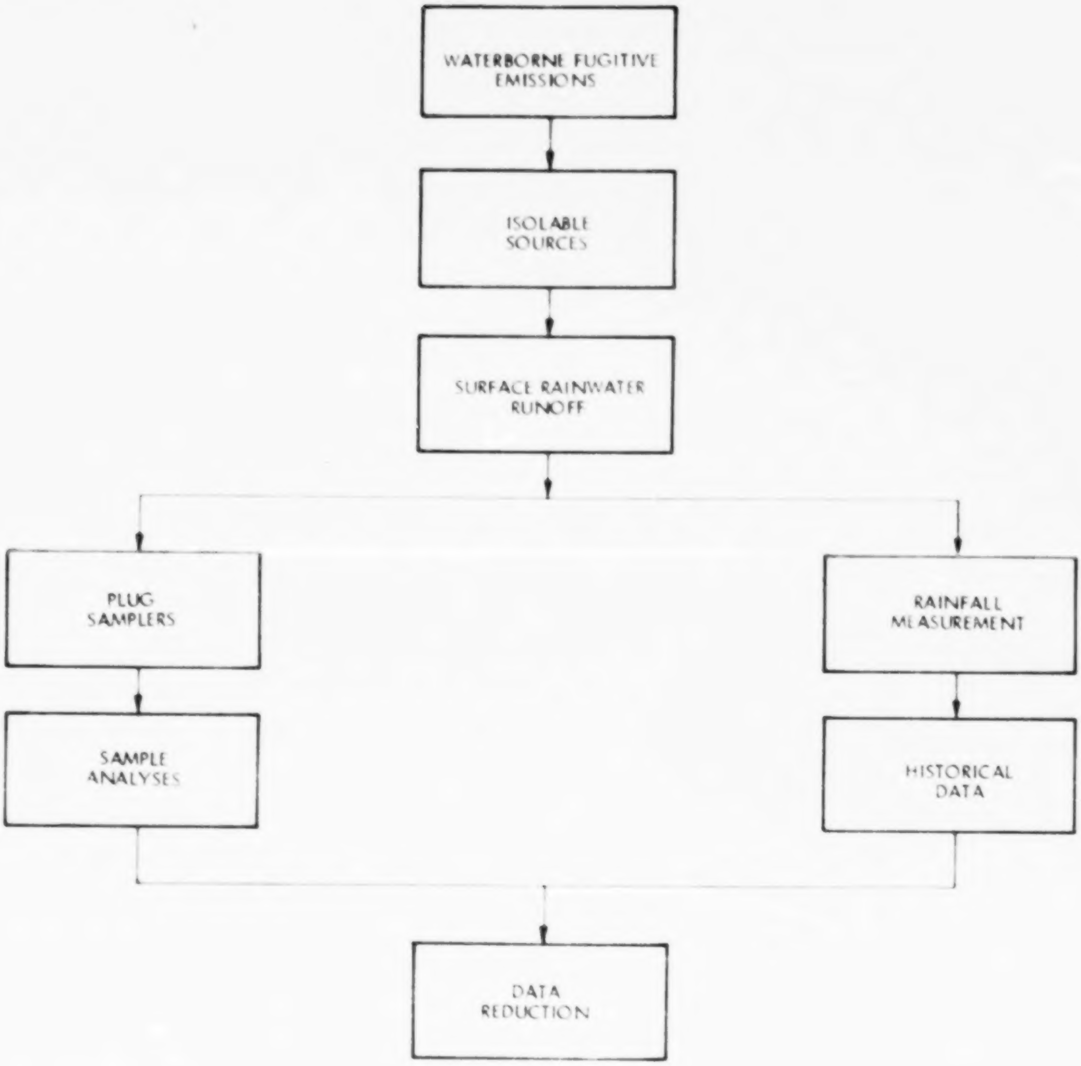


Figure 20. Level 1 Water Runoff Fugitive Emissions Characterization

CHAPTER V

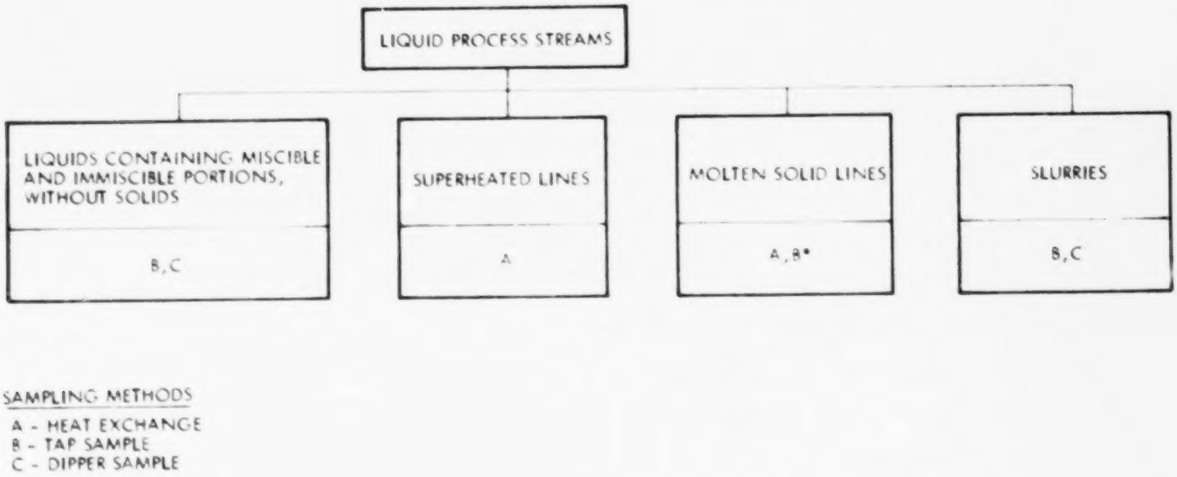
LIQUID AND SLURRY SAMPLING

5.1 INTRODUCTION

In any given industrial process operation, the probability is high that a number of the influent and/or effluent streams will exist in liquid or slurry form. Considering the multiplicity of liquid or slurry streams in typical plants, the number of possible sampling points becomes extensive.

Figure 21 summarizes the types of streams generally found in industrial operations and the sampling methods to be used. It should be noted that these streams are transported in a variety of ways which may range from closed pipes to open ditches and sluices. The three methods chosen for the Level 1 sampling of liquids and slurries are heat exchange, tap sampling and dipper sampling. Each method is discussed in detail in Section 5.3.

Once the samples are collected, they may be analyzed on site or packaged for shipment and analysis at the laboratory (see Chapters VII and



*TAP SAMPLE MAY BE TAKEN IN LINES OF THIS NATURE ONLY IF THE MATERIAL IS LIQUID AT RELATIVELY LOW TEMPERATURES (i.e., CERTAIN PETROLEUM TYPES)

Figure 21. Sampling Methods as a Function of Stream Type

VIII). Streams may be organic or aqueous or may contain water/organics/ solids in miscible or immiscible fractions. The handling of these solutions will affect the reliability of the chemical or biological tests performed. Section 5.4 proposes a tentative field separation scheme to prevent sample loss or adulteration. This scheme is comprehensive enough to prevent sample loss, but is simple enough to implement in the field.

5.2 PREPARING FOR SAMPLE COLLECTION

5.2.1 Pre-Test Site Survey

The same criteria for locating a gas sampling point can be applied to locating sampling sites for liquid samples. A review of those criteria and procedures is contained in Section 2.2, Chapter II.

While the site selection criteria for gas and liquid sampling are generally the same, the test personnel must be aware of the problems associated with the sampling of liquids and how these factors affect the choice of a sampling site. Two factors will affect the selection of a sampling site for liquid/slurry streams:

- Stream Homogeneity - This is the most important problem that must be addressed by the site survey crew. Unlike gas streams which mix fairly evenly, liquid streams tend to be more stratified because of lower thermal agitation and higher fluid viscosities.

- Stream Flowrate - Large, slow-moving streams will offer more of a chance for stratification to occur. This factor is especially important in large pipes or open sluices and ditches.

These factors indicate that free-flowing streams should be sampled after points of turbulence (elbows) to collect samples of maximum homogeneity. Because of the possible stratification in slow moving open streams, a sampling point should be chosen so that a full stream cut can be made with a dipper sampler. Sluice gates or pipe outfalls offer a good opportunity to obtain a sample in this fashion.

In all cases the main pipe or stream flow should be sampled. Because solids can accumulate in seldom-used vent or slip streams, these lines are not recommended for sample acquisition. Long slip stream lines are to be avoided, but can be used if the main line is inaccessible and if the slip stream line is flushed with several times the volume of liquid held in the line between the main line and the tap.

5.2.2 Personnel Requirements

The liquid and slurry sampling techniques presented in this chapter are uncomplicated, and under favorable conditions only one person is needed to perform the sampling effort. There are conditions, however, where additional manpower will be required. Many streams will require that a crew member work under conditions or in areas where the potential for physical mishaps is high. For example, using a dipper to sample an open stream might require a crew member to extend himself physically to reach the sampling point either by leaning from catwalks, reaching from ditch banks, or physically wading in the stream. In other cases, the closed stream will be under high pressure and temperature which will multiply the dangers involved in taking a sample. An additional crew member should be present here to ensure the safe completion of the task even though his active presence is not necessary for the sampling effort.

5.2.3 Equipment Preparation

5.2.3.1 Sample Containers

Containers intended for sampling industrial water streams must be made of a high density polyethylene or polypropylene. Plastic bottles for aqueous stream samples should be cleaned by:

a) Detergent wash, followed by
b) Distilled water rinse, followed by
c) 1:1 sulfuric and nitric acid mix.

Organic samples, including CH_2Cl_2 extractions, must be placed in amber glass bottles to inhibit sample degradation. These amber glass bottles are cleaned by:

a) Strong soap solution,
b) Liberal tap water rinse,
c) Distilled water rinse,
d) Methanol rinse,
e) Methylene chloride rinse, and
f) Drying a clean, hot air stream or by placing in an oven at 40°C (140°F).

After the apparatus has been cleaned and dried, it should be stored in boxes to prevent spurious contamination.

5.2.3.2 Apparatus

Sampling lines should be as short as possible to facilitate flushing and to reduce time lag. The lines must have sufficient strength to prevent structural failures. Lines intended for sampling streams under pressure must be designed in accordance with the specifications outlined in the American Standard Code for Pressure Piping. Where small diameter capillary tubing is used, it should be protected by a sheath of larger diameter pipe of adequate structural strength. Materials of construction should conform to the applicable specifications of the American Society for Testing and Materials as follows:

- Pipe (seamless ferritic alloy-steel for high temperature service) - ASTM Designation A335.
- Tubing (seamless carbon-steel for high temperature service) - ASTM Designation A179.
- Tubing (seamless alloy-steel for high temperature service) - ASTM Designation A608.

Valves and fittings must be fabricated from materials similar to those used in the sampling lines and must also conform to the requirements of the specifications of the American Society for Testing and Materials as follows:

- Steel (suitable for fusion welding up to 850°F) - ASTM Designation A216.
- Steel (carbon forged) - ASTM Designation A105.
- Steel (alloy steel castings for use up to 1100°F) - ASTM Designation A217.

Materials for fabrication of sampling apparatus not intended for use in pressure applications are not required to meet such stringent specifications due to the significantly reduced safety requirements. The primary element of importance here is the fabrication of equipment from materials which will not contaminate the sample. It is preferable, therefore, that the sampling lines and collection reservoirs used for sampling liquid streams be made of Teflon because of its superior chemical inertness toward strong acids, alkalis, and other chemical reagents.

All portions of the sampling apparatus which come into contact with the sampled stream should be cleaned using the same procedure that was used in cleaning the container for that sample (see Section 5.2.3.1).

5.3 SAMPLING PROCEDURES (References 42, 43)

As indicated in Figure 21, all liquid and slurry streams can be divided into distinct sub-groups, each defined as a function of the physical makeup of the stream. Each stream, having been so identified, may be assigned a sampling procedure applicable to that stream type. As indicated in Figure 21, three specific methods are applicable; they are:

a) Heat exchange,
b) Tap sampling, and
c) Dipper sampling.

Where the stream to be sampled exists at a pressure high enough above atmospheric to provide an adequate sample flow rate, the removal of the sample presents no problem. At near atmospheric pressures, special means must be provided to establish sample flow. This problem can be overcome by using either a small pump to deliver the sample to the sample container or an evacuated sampling vessel. Prior to sample acquisition, all new sampling lines should be purged with line fluid to remove any deposits in the system lines and to condition the sampling lines. The period of time required will depend on the system line size and distance from the main stream. Once the lines have been flushed, sampling can begin. A 10-liter sample is required to perform the analyses identified in Chapters VII and VIII.

5.3.1 Heat Exchange Sampling Systems for High Temperature Lines

The majority of industrial systems utilize steam for a variety of process applications ranging from relatively clean power plant operations to polluted lines resulting from stripping operations involving acid units, catalyst regeneration and scrubbing of polluted gas streams. In addition to pressurized process lines, various other process operations exist which contain superheated vapors composed of effluents generally characterizable as reaction products. The sampling techniques described in this section pertain to all of the above systems; however, for the sake of brevity, the term HT line (high temperature) will be used to represent all applications, unless otherwise indicated.

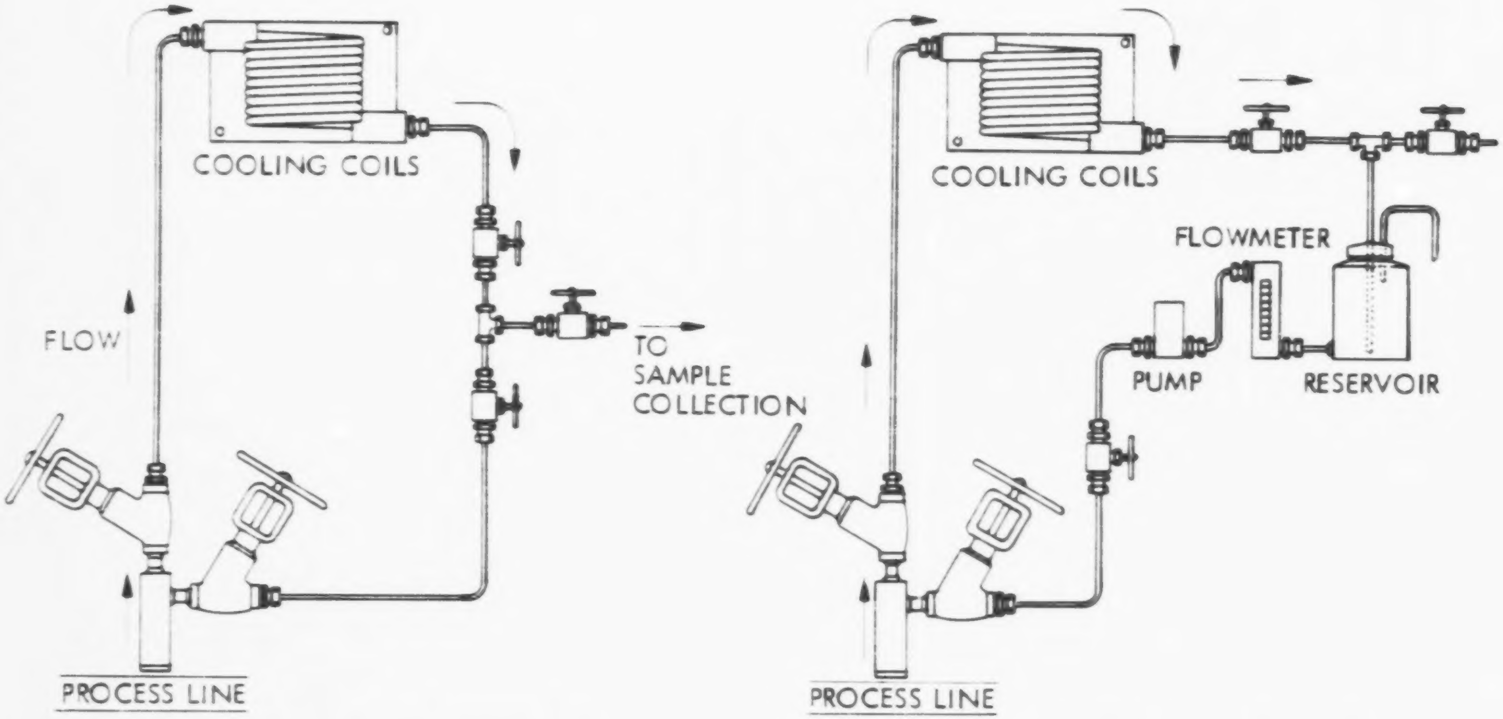
The principle used in the sampling of HT lines involves the use of a water-cooled condenser system. Typical examples of apparatus used for this purpose are illustrated in Figure 22. As can be seen in Figure 22, two approaches are possible depending on whether the pressure in the line is above or below atmospheric pressure. The condensate from the stream is collected in a reservoir for later analysis.

In sampling HT lines, it should be kept in mind that stream constituents will to some degree dissolve any substance contacted. For this reason, the area of the surfaces exposed to the sample and the time that the sample is in contact with these surfaces should be kept to a minimum.

As indicated earlier in paragraph 5.2.3.2, all tubing, valves, nozzles, and containers must be constructed from materials of sufficient strength to withstand the full pressure of the stream being sampled. Tubing diameter must be small enough so that storage within coils and tubing and the resultant time lag of the sample through the system are minimal. The sampling operations presented in this section may be used with complete safety provided that proper caution is exercised.

5.3.2 Tap Sampling (Reference 44)

Contained liquids may be divided into two broad categories: those which are in motion (lines) and those which are not (tanks or drums). Usually, a specific sampling technique is applied to each of the above two categories in order to accommodate the differences in sample characteristics, such as stratification. A flowing stream containing particulate matter will be stratified. A tank sample may also be stratified but in the static sense rather than in the fluid sense. Moving streams are traditionally sampled using a technique called continuous sampling. This involves sample removal from a tap which is connected to a probe inserted into the line. Static liquid samples (tanks or large drums) are sampled using a technique called tap sampling.



NATURAL CIRCULATION SAMPLING SYSTEM
(HIGH PRESSURE, HIGH TEMPERATURE)

FORCED INJECTION SAMPLING SYSTEM
(SUBATMOSPHERIC PRESSURE, HIGH TEMPERATURE)

Figure 22. Sampling Apparatus for HPHT Lines

For the purposes of Level 1, the effort of inserting a probe into the line is too time-consuming to be efficient. Consequently, all contained liquids will be sampled using the tap method, as per ASTM D-270 (Ref. 44).

Tap sampling, as described in this chapter, describes a wide variety of grab techniques. In general, this type of sampling implies that a sample is taken at a tap from a line or tank wall. This approach is used for moving liquid or slurry streams. The procedure is also applicable to streams under pressure or elevated temperature provided that the proper safety precautions are exercised. For systems under pressure, lines should be cracked very slowly to avoid injury caused by sudden surge due to entrained air pockets or accumulated solids around the valve opening. Streams under elevated temperatures should be sampled using a heat exchanger system such as is described in ASTM D-270 (Ref. 44).

Tap samples are collected by inserting the sample line (a thoroughly washed Teflon line) into the sampling bottle so that it touches the bottom. (After first flushing the sample line at a rate high enough to remove all sediment and gas pockets.) The sample bottle should be thoroughly rinsed with sample prior to filling and the sample line flow must be regulated so as not to exceed 500 ml/min. If sampling valves or stopcocks are not available, samples may be taken from water-level or gage-glass drain lines or petcocks.

5.3.3 Dipper Sampling

The dipper sampling procedure is applicable to sampling sluices or open discharge streams of thick slurry or stratified composition. The dipper is made with a flared bowl and attached handle, long enough to reach the sluice or discharge areas. The bowl portion must be coated with Teflon.

A dipper sample is obtained by inserting the dipper into the free-flowing stream so that a portion is collected from the full cross-section of the stream. Sample portions are to be taken at time intervals chosen so that a complete sample is collected which is proportional to the pumped quantity. The gross amount of sample collected should be approximately 0.1 percent, but not more than 40 gallons, of the total quantity being sampled. As noted previously, this should be at least 10 liters or reduced to that quantity for analysis.

Although it is generally agreed that time-integrated sampling techniques are too sophisticated for Level 1 application, the lack in uniformity often found in thick or stratified slurries may require special consideration in some cases. The site survey will produce information on process cycles so that the sampling times and points cover the most representative period and location of discharge.

5.4 LIQUID SAMPLE HANDLING AND SHIPMENT

As mentioned previously in Section 5.1, sample handling is an important consideration where liquids are involved. The entire spectrum of liquid samples exists within the bounds of the following six categories:

1) Aqueous
2) Aqueous/organic
3) Organic
4) Aqueous/solid
5) Organic/solid
6) Aqueous/organic/solid.

These samples must be stabilized prior to shipment for laboratory analysis. Figure 23 shows a field handling scheme for liquid/slurry samples. This scheme has been modified (Ref. 45) to handle suspended particulate matter. Figure 23 shows the worst case (Aqueous/Organic/Solid), but is also applicable to the simpler cases.

It is recommended that in-field separations and specific preservation techniques, rather than a general all-purpose approach that is not specific for inorganic, organic and biological preservation, be followed. Table 3 outlines the application of Figure 23 to less complicated systems. It should be noted that both BOD and COD samples are typically taken before filtration. Sulfite should be determined in the field and as soon as the samples are returned to the lab.

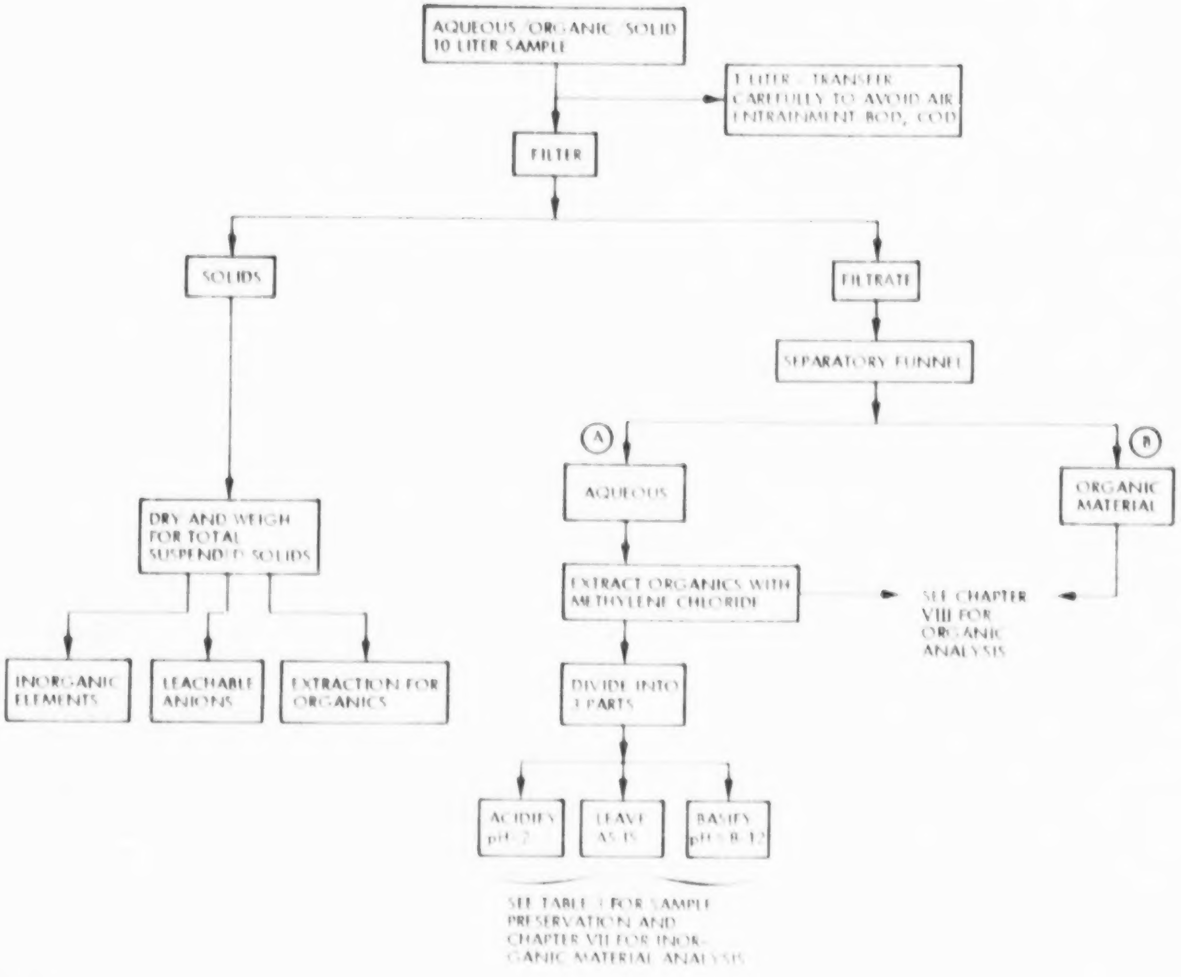

AQUEOUS/ORGANIC/SOLID 10 LITER SAMPLE
1 LITER - TRANSFER CAREFULLY TO AVOID AIR ENTRAINMENT BOD, COD
FILTER
SOLIDS
FILTRATE
SEPARATORY FUNNEL
A
B
AQUEOUS
ORGANIC MATERIAL
DRY AND WEIGH FOR TOTAL SUSPENDED SOLIDS
EXTRACT ORGANICS WITH METHYLENE CHLORIDE
SEE CHAPTER VIII FOR ORGANIC ANALYSIS
INORGANIC ELEMENTS
LEACHABLE ANIONS
EXTRACTION FOR ORGANICS
DIVIDE INTO 3 PARTS
ACIDIFY pH < 2
LEAVE AS IS
BASIFY pH > 8-12
SEE TABLE 3 FOR SAMPLE PRESERVATION AND CHAPTER VII FOR INORGANIC MATERIAL ANALYSIS

Figure 23. Field Handling Scheme for Liquid/Slurry Samples

Table 3. List of Analyses to be Performed on Liquid/Slurry Samples.

Analysis	Field Analysis	Lab Analysis	Fraction	Preservation	Holding
Acidity	✓		Untreated	Cool 4°C	24 hrs
Alkalinity	✓		Untreated	Cool 4°C	24 hrs
Conductivity	✓		Untreated	Cool 4°C	24 hrs
BOD	✓		Untreated	Cool 4°C	6 hrs
COD		✓	Acidify	H_2SO_4 to pH <2	7 days
Suspended Solids		✓	Untreated	None Required	-
Total Dissolved Solids	✓		Untreated	None Required	-
Hardness	✓		Untreated	Cool 4°C	7 days
Water & HCl Leachable Anions		✓	Basify	NaOH to pH12	Depends on Anion
Trace Cations		✓	Acidify	HNO_3 <2	38 days
pH	✓		Untreated	Run Immediately	38 days
Organic Material		✓	Untreated	None Required	7 days
Methylene Chloride Extracts		✓	Untreated	Non Required	7 days
Cyanides	✓		Untreated	Cool 4°C	24 hrs
Ammonia Nitrogen	✓		Untreated	Cool 4°C	24 hrs

CHAPTER VI

SOLID SAMPLING

6.1 INTRODUCTION (References 46, 47)

Solid sampling covers a broad spectrum of material sizes from large lumps to fine powders and dusts. There is an equally diverse assortment of potential sample sites including railroad cars, barges, trucks, large heaps, plant hoppers and conveyor belts. Obviously, no one sampling method or piece of equipment can accommodate all possible situations. Furthermore, all of the above sampling locations may contain products of widely varying consistency. For the purposes of this chapter, the consistency of solid samples ranges by definition from anhydrous or dry solids to thick, nonflowing pastes.

The recommended Level 1 sampling technique is the grab sample. In general, the Level 1 and Level 2 solid sampling techniques are identical except that in the case of Level 2 sampling a series of grab samples is taken over a period of time from a conveyor belt or over a larger area for stationary storage sites such as railroad cars or large heaps. In cases of extreme sample variability, a larger grab sample consisting of several increments or shovelfuls is required on Level 1. In most cases, the difference between the Level 1 sample and a time-averaged Level 2 sample is only a matter of degree rather than of technique.

The following sections present the sampling approaches applicable to input and output solid streams and storage piles.

6.2 PRE-TEST SITE SURVEY (References 8, 48)

Solid input and output streams in most process operations consist of fuels, primary reaction components, treatment or maintenance chemicals, salable output products or output refuse products. These solids range from very fine powders to very coarse lumps. This variation in sample consistency influences the sampling technique to be used which must be established in the pre-site survey. For the purpose of the pre-test site survey, therefore, the following questions must be answered:

1) Can the material be sampled as it enters or leaves the process, or must it be sampled in its storage or pile form?

2) If the material can be sampled as it enters or leaves the process, what is the nature of the conveyor system (belt, worm screw, duct) and what is closest available sampling location to process entry, and farthest available sampling location from process exit?

3) What is the consistency of the material (powder, coarse grain, lump) and what is the apparent variance within this consistency, and

4) What is the approximate size of the storage reserve and what is the method of access to said reserve?

Each of these parameters must be identified before the procedures in the following section can be adequately implemented.

6.3 SOLIDS SAMPLING PROCEDURES

Level 1 solid sampling procedures use three manual grab sampling techniques: shovel or grab sampling, boring techniques, which include pipe or thief sampling; and auger sampling. Data obtained from the pretest site survey concerning the physical characteristics of the sample, together with the optimum choice of sampling location will determine the appropriate sampling technique. Table 4 presents a sampling matrix showing the appropriate sampling technique as a function of physical characteristics and actual location of the sampling points.

Each of the grab sampling techniques is discussed in detail in the sections to follow.

6.3.1 Shovel Grab Sampling (References 20, 22, 47, 49)

Raw material piles of relatively coarse lump size (ore piles, aggregate piles, coal feed, etc.) are sampled using a fractional shoveling technique. The shovel used in this procedure is of the square-edged variety measuring 12 inches wide.

In sampling from belt conveyors, one full cross-section the width of the shovel blade is taken as the sample.

Where ladder or tray conveyors are sampled, one shovelful from one compartment is removed.

Table 4. Decision Matrix for Solid Sampling

PHYSICAL NATURE OF SAMPLE	BELT CONVEYORS	LADDER TRAY CONVEYOR	SCREW CONVEYOR	DUCT SAMPLE	OPEN PILES	STORAGE BINS OR SILOS
FINE POWDER	N/A	SHOVEL GRAB FROM ONE TRAY	ONE SHOVEL FROM POINT OF EXIT	ONE SHOVEL FROM EXIT IF ENCLOSED, FROM TOP IF OPEN	PIPE OR THIEF	PIPE OR THIEF
COARSE POWDER	N/A	SHOVEL GRAB FROM ONE TRAY	ONE SHOVEL FROM POINT OF EXIT	ONE SHOVEL FROM EXIT IF ENCLOSED, FROM TOP IF OPEN	PIPE, THIEF OR AUGER	PIPE, THIEF OR AUGER
COARSE GRAIN	CROSS STEAM CUT, ONE SHOVEL	SHOVEL GRAB FROM ONE TRAY	N/A	ONE SHOVEL FROM EXIT IF ENCLOSED, FROM TOP IF OPEN	AUGER	AUGER
LUMP	CROSS STEAM CUT, ONE SHOVEL	N/A	N/A	N/A	FOUR SHOVELS, ONE FROM EACH SIDE	SHOVEL OR AUGER

Screw conveyors transfer sludge-type materials (such as ash effluents) and are usually enclosed systems. The optimum sampling point for these systems is the content exit. If this point is located in an unreachable position, the sample must then be withdrawn from the entrance or exit area, depending on whether the stream is influent or effluent using a pipe, thief or auger technique (Section 6.3.2).

Duct conveyors consist of either gravity feed systems or chaindrive scrapers and may be open top or enclosed depending on the fineness of the solid being transported. Open duct conveyors are sampled by removing one shovelful of material from the top from the adjoining catwalk. Closed ducts are sampled by taking one shovelful from the exit point. If these points are unreachable, the sample must be taken from the storage pile using a pipe, thief or auger (Section 6.3.2).

6.3.2 Boring Techniques (References 22, 46, 50)

Pipe borers represent another class of solid sampling methods applicable to materials stored in piles, silos or bins. The pipe is inserted into the material to be sampled at regular intervals. The method is fairly reliable, providing that the pipe is long enough to reach the bottom of the material. However, it is only applicable to fine or powdered dry materials, because lumps or any stickiness will jam or plug the pipe. Small pipe borers can be used to sample material in sacks or cans. There are primarily two pipe designs that give best results. One is a simple pipe that is tapered so the end first inserted is smaller in diameter than the handle end. A more sophisticated design, known as a thief, makes the sample more representative vertically. It consists of two close-fitting concentric pipes sealed at the base in a conical point. Longitudinal slots are cut along the side of each pipe. The thief is inserted with the slots turned away from each other and then, when the sampler is in position, the outer pipe is rotated, lining up the slots and allowing the inner pipe to fill with sample. For proper results with any design of pipe borer, the opening through which the sample material passes (slots or circular pipe ends) must be larger than the largest particle size.

Auger samplers, a form of drill, pack the sample in the helical groove of the auger and can be enclosed in a casing if the nature of the sample is such that it will spill when the auger is removed from the hole. Like pipe borers, they are simple to use and have the further advantage of being applicable to a greater variety of materials. For example, augers work well for materials that are packed too hard for the insertion of a pipe sampler. For very packed materials, machine-driven augers are available. However, if spillage is a serious problem, a thief type pipe sampler is the better choice.

6.4 SAMPLE COLLECTION AND STORAGE (References 3, 20, 21, 60)

It is always preferable to sample a moving stream either in pipes or off conveyor belts rather than stationary storage sites. This is particularly true if the sample has a wide particle size distribution. Stored containers or heaped beds of material tend to settle, segregating the particles according to size and density, and it is difficult to compensate for this bias during sampling. Furthermore, large masses of stored material are extremely difficult to handle. The interior portions are relatively inaccessible, and the amount of time and space needed to move the material enough to take a representative sample can become prohibitive. However, such situations can generally be avoided by a good sampling test plan.

Typically in a process test for trace elements the solid materials of interest are the feed materials and the residues from particulate matter scrubbers such as baghouses, high energy venturis, and electrostatic precipitators. Raw feed stock as it passes through the process stream may pick up other materials as contaminants and therefore differs greatly in composition from the final feed to the process. Consequently, samples should be taken at the last possible site before the stream is fed into the process. This means that sampling will generally be conducted from a feed hopper, if accessible, or from the pipes or conveyors which feed the materials to the process. Similarly, scrubber residues can be sampled from the collection hopper or from pipes going to the hopper. Extra handling steps only increase the chances of the sample becoming contaminated.

When samples are taken from conveyor belts, the standard procedure is to stop the conveyor at regular intervals (e.g., every 10 or 15 minutes) and shovel off a section of the material. Flat-nosed shovels with straight perpendicular sides are best for this type of sampling.

Samples collected in accordance with the above prescribed procedures should be stored in air-tight, high density polyethylene containers until ready for analysis. Large samples should be placed in metal containers lined with polyethylene bags.

CHAPTER VII

LEVEL 1 INORGANIC ANALYSIS TECHNIQUES

7.1 INTRODUCTION (References 1, 2, 51)

Sampling and analytical programs can at a minimum be divided into three distinct categories. The first category is compliance testing where the procedures along with their precision are delineated in the Federal Register. A second type of sampling and analytical program is designed to support specific R&D programs and the precision and accuracy of the data are defined by its end uses. The third type of program is designed to provide information which can be utilized in each of the specific levels of a phased environmental assessment.

In respect to the Level 1 environmental assessment as described in this manual, a goal for precision and accuracy within a factor of two to three of the rate of input and emission composition is desired. To achieve this goal, the analytical results must have an accuracy of -50 to +100 percent assuming a sampling accuracy of -50 to 100 percent (Section 1.5).

Samples obtained in accordance with the procedures outlined in the preceding chapters will be either gases, liquids, or solids. The multimedia analysis flow scheme presented in Figure 24 represents the way in which each of the sample types is split for organic and inorganic analysis. The inorganic analysis scheme is detailed in a companion flow diagram (Figure 25).

The analytical methods chosen for this manual are the recommended techniques for Level 1 determinations. They represent the optimum approach to an integrated multimedia assessment effort and should be considered comprehensively rather than independently. For example, on-site GC is identified for general Level 1 inorganic gas analysis. Viewed independently, a variety of alternative techniques will provide satisfactory Level 1 data for inorganic gases; yet within the integrated Level 1 analysis format, the GC can also be used for organic gases and consequently becomes the optimum choice.

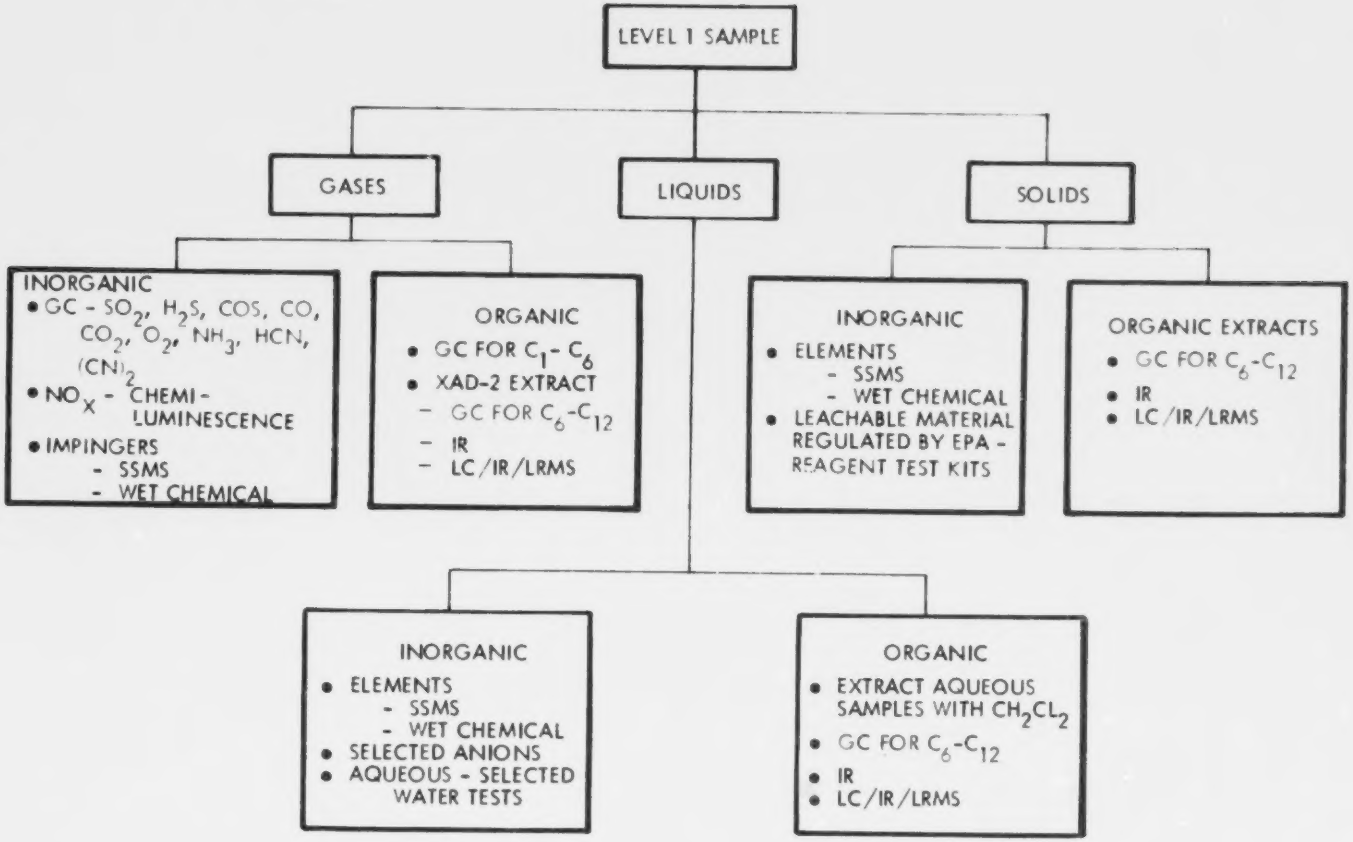


Figure 24. Multimedia Analysis Overview

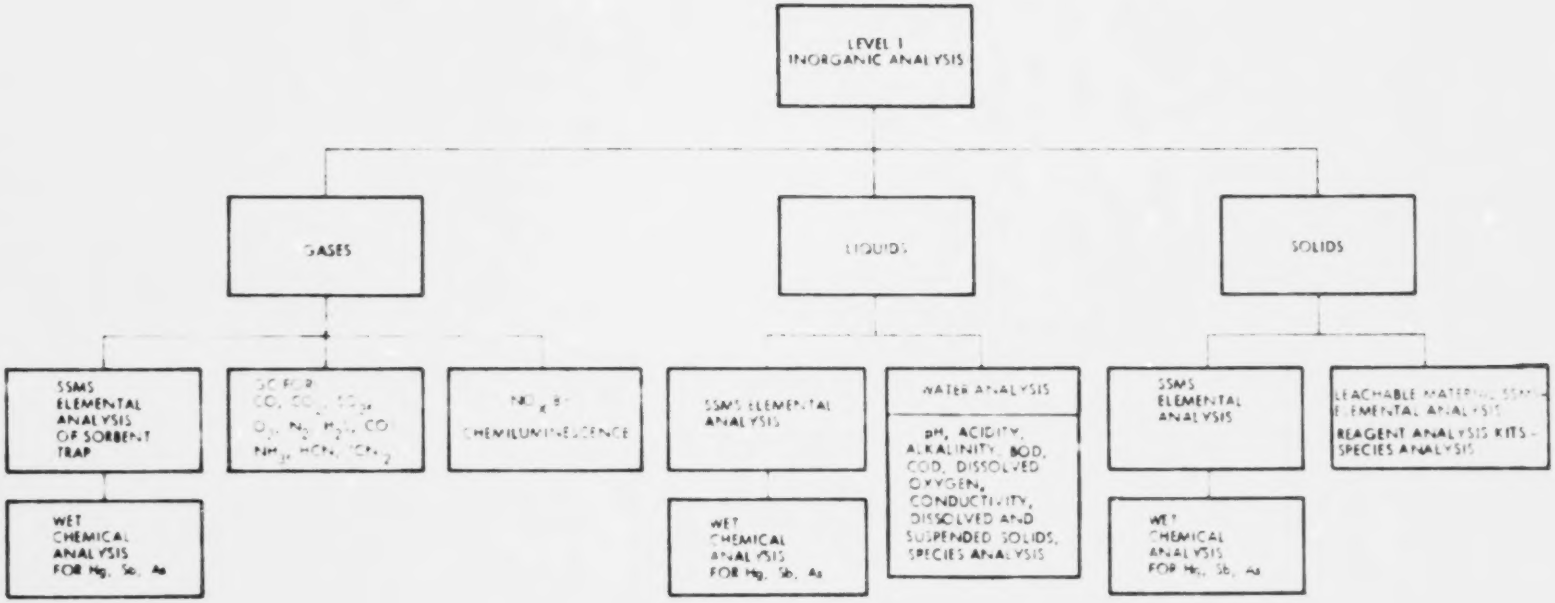


Figure 25. Level 1 Inorganic Analysis Flow Scheme

Level 1 samples are analyzed without making assumptions regarding the content of any given sample. Consequently, the analysis plan is designed to create a network capable of screening all incoming samples in such a way that no environmentally significant element or species escape undetected. This "screening network" applied to Level 1 inorganic analysis is designed to detect:

- Inorganic elements in all influent and effluent streams,
- SO_2, NO_x, CO, O_2, CO_2, N_2, H_2S, COS, NH_3, HCN and $(CN)_2$ in gaseous streams,
- pH, acidity, alkalinity, conductivity, BOD, COD, dissolved oxygen, dissolved solids, and suspended solids in water streams in addition to inorganic elements, and
- Leachable cations and anions from samples which are solids (particulate matter from SASS, slurry solids, etc.)

In this way, environmentally important components or streams are identified and prioritized so that the Level 2 effort can be directed to the most environmentally significant streams.

The following sections in this chapter describe special considerations in the analysis of Level 1 samples.

7.2 LEVEL 1 ANALYSIS METHODOLOGY

The analysis of samples from the Level 1 sampling effort will require the use of methods applicable to gases, liquids and solids. Solids and liquids will be analyzed for elements including the halogens by spark source mass spectrometry (SSMS) after the proper sample preparation. Liquids will be analyzed directly for complex anions using reagent test kits (Hach or Bausch and Lomb) either in the field or in the laboratory (see Table 3, pg. 75). These same reagent kits will be used to analyze the leach solutions from the solid samples. Gas samples will be analyzed on site for inorganic components by gas chromatography (GC). The following paragraphs discuss the application of these analysis approaches to the samples collected.

7.2.1 Elemental Analysis by Spark Source Mass Spectrometry (References 52 through 62)

There are two general types of SSMS detection systems: photographic plate, and electrical detection. For Level 1 survey purposes, the photographic system using the "just disappearing line" technique will be applied. To achieve the highest sensitivity, a series of exposures of the photoplate is made using the sample, followed by a series of exposures with a reference sample. Precision and accuracy are highly dependent on spectral line widths and shapes. These parameters define optical densities which are converted to ion densities by means of calibration curves. A number of computer-oriented systems for the derivation and integration of ion intensity profiles have been developed for use in accurate and precise determinations.

Four specific groups of samples for inorganic element analysis result from a Level 1 sampling survey:

1) XAD-2 trap,
2) Aqueous samples,
3) Organic samples (liquid or solid), and
4) Particulate matter, including probe and cyclone washes and ash samples.

In order to analyze these samples for trace elements by SSMS, two general sample conditions must be met:

1) The sample, if it is not a conductor, must be placed into a conducting medium (graphite), and
2) The sample must be as free as possible from organic matter which can complicate spectra interpretation.

Figure 26 shows in schematic form how each sample type is prepared to meet these conditions; further explanation is given in the following paragraphs.

Aqueous liquid samples can meet the two conditions simply by adding a small amount of the sample to powdered graphite and allowing the water to evaporate. (One ml of solution is needed to obtain a 1 ug/l sensitivity assuming a basic SSMS sensitivity of 10^{-9}g.) The graphite is then pressed into an electrode. Particulate matter, ash, and fuels will require more

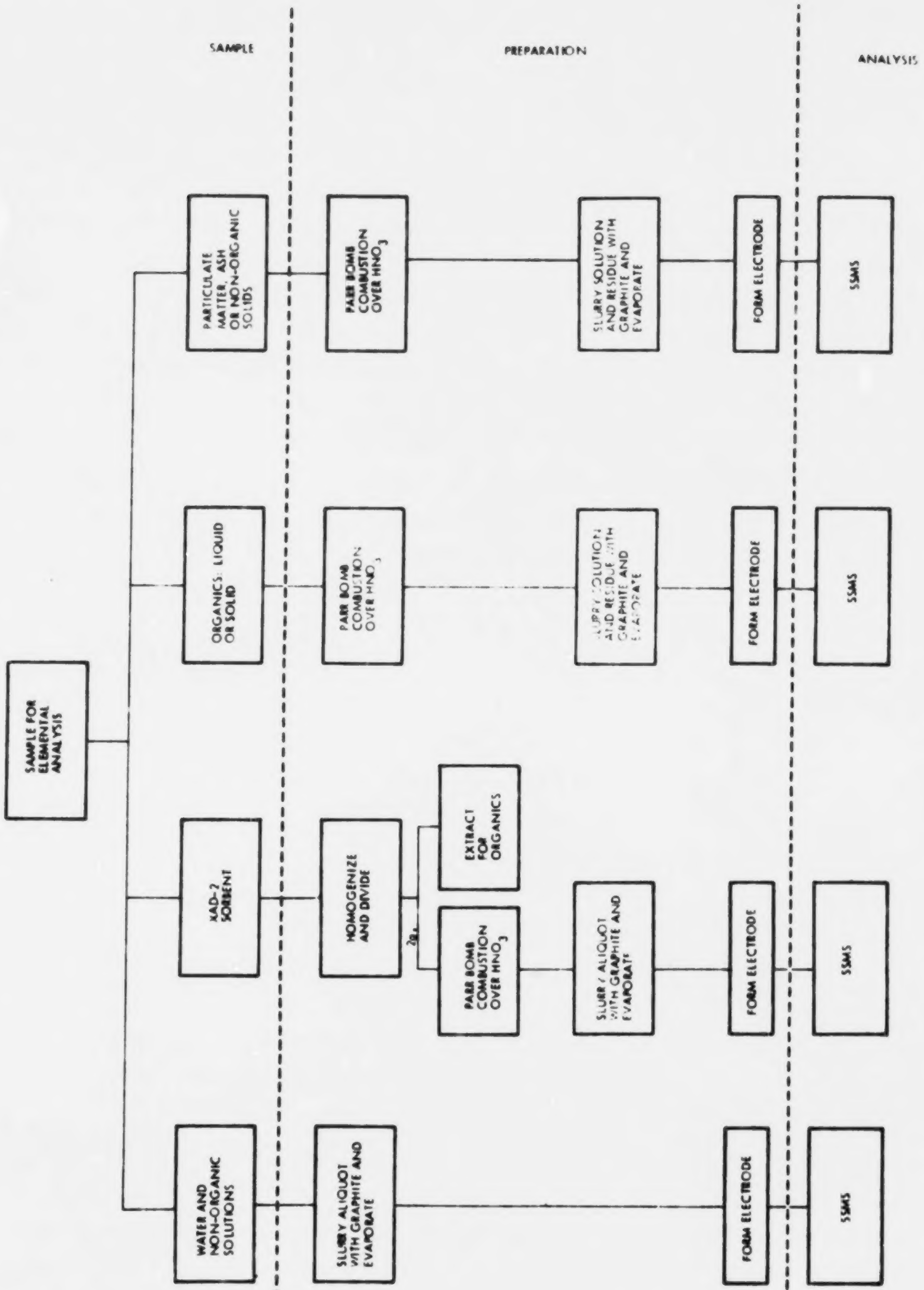

SAMPLE
PREPARATION
ANALYSIS
SAMPLE FOR ELEMENTAL ANALYSIS
WATER AND NON-ORGANIC SOLUTIONS
XAD-2 SORBENT
ORGANICS: LIQUID OR SOLID
PARTICULATE MATTER, ASH OR NON-ORGANIC SOLIDS
SLURRY ALIQUOT WITH GRAPHITE AND EVAPORATE
HOMOGENIZE AND DIVIDE
2g
PARR BOMB COMBUSTION OVER HNO$_3$
EXTRACT FOR ORGANICS
PARR BOMB COMBUSTION OVER HNO$_3$
PARR BOMB COMBUSTION OVER HNO$_3$
SLURRY ALIQUOT WITH GRAPHITE AND EVAPORATE
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
FORM ELECTRODE
FORM ELECTRODE
FORM ELECTRODE
FORM ELECTRODE
SSMS
SSMS
SSMS
SSMS

Figure 26. Sample Preparation for SSMS Elemental Analysis

extensive preparations consisting of reducing the organic material content of the matrix. This matrix reduction step consists of ashing the sample by Parr bomb combustion of the sample over HNO_3. An aliquot of this sample is then formed into an electrode in the same manner as the aqueous samples.

Analysis of the XAD-2 sorbent trap for trace elements is a unique problem because little is known about volatile element retention of the sorbent trap. In addition, adsorption is not uniform throughout the length of the trap. For this reason, the XAD-2 sorbent is first thoroughly mixed to ensure a homogeneous sample, and then a 2 g aliquot of the sorbent is used in a Parr bomb combustion over HNO_3. The inorganic elements are then determined by SSMS, and the remainder of the sample is then used for organic analysis (Chapter VIII.)

7.2.2 Wet Chemical Analysis for Hg, As and Sb (References 63, 64)

While SSMS can theoretically analyze any element, it has been found in practice that Hg, As, and Sb are analyzed poorly by SSMS. Thus, these elements are determined by atomic absorption spectroscopy (AAS) or wet chemicals methods. Figure 27 summarizes the analysis scheme for Hg, As, and Sb for each of the four general types of samples. This scheme presents the dissolution techniques for the various samples so that once the sample is in solution, the appropriate AAS or colorimetric procedures can be performed.

Since several additional sample preparation steps are included in the analysis scheme, care must be taken to avoid contamination. Clean working areas set aside for trace material analysis are required. Reagent blanks on all solutions, acids and reagents must be run to ensure accurate results.

Analysis of water, particulate matter, ash and fuels for Hg, As, and Sb is accomplished with well known analysis schemes. In the XAD-2 analysis, the samples are treated as fuels and bomb combusted. These analyses have few interferences.

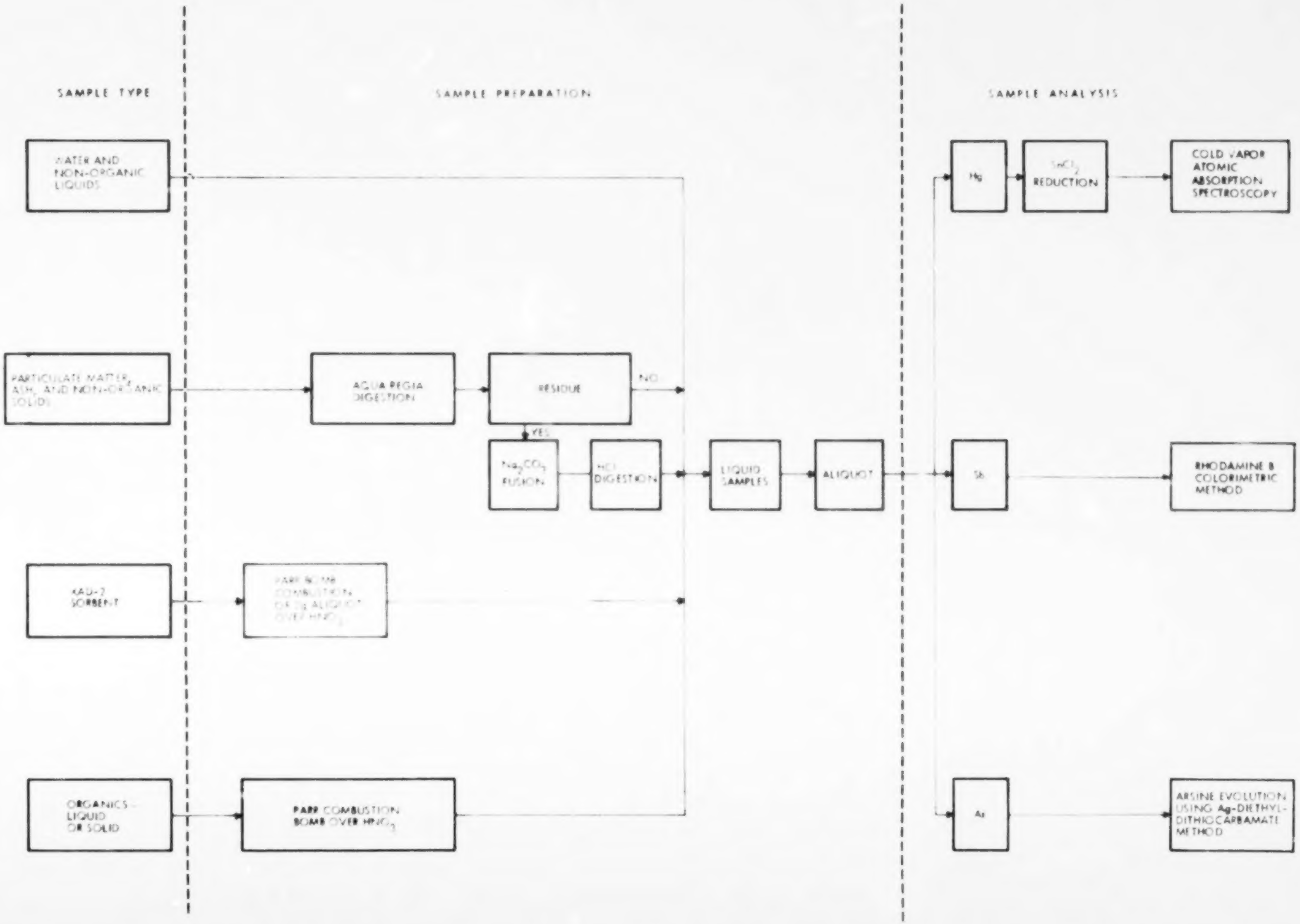

SAMPLE TYPE
SAMPLE PREPARATION
SAMPLE ANALYSIS
WATER AND NON-ORGANIC LIQUIDS
PARTICULATE MATTER, ASH, AND NON-ORGANIC SOLIDS
XAD-2 SORBENT
ORGANICS - LIQUID OR SOLID
AQUA REGIA DIGESTION
RESIDUE
NO
YES
Na_2CO_3 FUSION
HCl DIGESTION
PARR BOMB COMBUSTION OF [illegible] ALIQUOT OVER HNO_3
PARR COMBUSTION BOMB OVER HNO_3
LIQUID SAMPLES
ALIQUOT
Hg
$SnCl_2$ REDUCTION
COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY
Sb
RHODAMINE B COLORIMETRIC METHOD
As
ARSINE EVOLUTION USING Ag-DIETHYL-DITHIOCARBAMATE METHOD

Figure 27. Hg, Sb, As Sample Preparation and Analysis

7.2.3 Gas Chromatographic Analysis of Gaseous Components

Gaseous samples to be analyzed will come from various sources including:

- Stacks,
- Vents,
- Process input streams,
- Process product streams, and
- Ambient air.

These samples must be analyzed for both inorganic and organic species over a span of concentrations ranging from sub-ppm levels for sulfur compounds to several percent for CO_2 and water in stack gas effluents. Because many of the samples which are taken, especially those which contain H_2S and other sulfur species, are unstable due to wall absorption or possible chemical reaction, it is recommended that the GC analysis be performed on site. This also eliminates the shipping of a potentially large number of bulky sample containers and permits additional sample taking if a problem area is identified.

Recent advances in gas chromatography have led to the development of sensitive and compact instruments that are practical for field applications. In addition, multidetector units such as those manufactured by Meloy, Beckmann, Tracor and others expand the scope of analysis to include virtually all gaseous species without having a van full of gas chromatographic units. It is recommended that a multidetector unit capable of detecting sulfur compound at the ppb level be purchased for an environmental assessment van.

Because no single unit is suitable for all proposed analyses, a set of columns, temperatures, and detectors is shown in Table 5. Organic species are shown because they will be present in most samples along with the inorganic species. It is not expected that the proposed set of conditions will be suitable for all mixtures and all possible concentration ranges. If a unique situation should arise, an alternative set of analysis conditions should be selected and submitted to the project officer and PMB-IERL-EPA for approval.

Table 5. Recommended Gas Chromatographic Parameters for Analysis of Inorganic and Organic Species

Species of Interest	Sensitivity	Column	Temperature	Detector
CO_2, CO, O_2, N_2, H_2O, SO_2^a, H_2S^a NO_x	1 ppm [a,b]	6 feet SS, Molecular Sieve 5A	Isothermal at 40°C	Thermal Conductivity
H_2S, SO_2, COS, CH_3SH, CH_3CH_2SH, -----, $C_6H_{13}SH$	1 ppb [c]	6 feet glass, 3% OV-1 on Chromosorb W, 100/120 mesh	Isothermal at 60°C	Flame Photometric
C_1-C_6 Hydrocarbons	0.1 ppm	6 feet SS, Poropak Q	Isothermal at 50°C	Flame Ionization
C_7-C_{12} Hydrocarbons	0.1 ppm	6 feet SS, 1.5% OV-101 on Gas Chrom Q, 100/120 Mesh	Isothermal at 50°C for 5 min; program at 10°C/min to 150°C	Flame Ionization
C_1-C_6 Chlorocarbons, Pesticides	0.1 ppm	6 feet SS, 1.5% OV-17/2.0% OV-210 on silanized Chrom W, H.P. or Gas Chrom Q 100/120 mesh	C_1-C_6 120°C Pesticides 200°C	Electron Capture
NH_3, HCN, Cyanogen	1 ppm	6 feet SS, Poropak Q	Isothermal at 40°C	Thermal Conductivity

a) Concentrations greater than 25 ppm only. For survey work and lower concentrations, the flame photometric detector system must be used.

b) Concentrations greater than 25 ppm only. For survey work and lower concentrations, the chemiluminescent method must be used.

c) A spectral Teflon-coated and glass system is necessary for these analyses.

The actual on-site analysis will be accomplished by using an evacuated vessel to sample the port, vent, or ambient air. This vessel will then be returned to the mobile van and attached to the gas chromatograph via an automatic gas sampling valve. The sampling vessel will automatically be sampled and the gas analyzed on the GC. The vessel can then be stored for further analysis back at the laboratory or purged, cleaned and evacuated for further use in the field.

7.2.4 Analysis of Nitrogen Oxides

Two gases of environmental interest (NO and NO_2) are not measured routinely on a gas chromatograph. The Level 1 analysis of NO/NO_2 concentrations will be performed using the chemiluminescence method. Although this is a state-of-the-art analysis technique, it is substantially less labor-intensive than EPA Method 7. This method as adapted to Level 1 analysis involves admitting gas samples into a 3-liter evacuated flask, as described in Chapter II. The sample is then transported to the instrument and analyzed. Because a major portion of the analysis time on the instrument involves calibration, it is recommended that only sufficient calibration to maintain a minimum accuracy of ± a factor of 2 (+100 percent, -50 percent) be performed.

7.2.5 Analysis of Leachable Material (Reference 25)

The analysis of water and HCl leachable material from solids can be performed by the standard procedures. Spark source mass spectrometry will be used for elements, halogens, and total sulfur, while reagent test kits will supplement SSMS by performing a variety of tests for complex anion species.

7.2.6 Analyses Specific for Aqueous Samples (References 37, 65, 66, 67, 68, 69)

In addition to the general inorganic elemental analysis specified in this chapter and the organic analysis specified in Chapter VIII, the following analyses must be performed on all aqueous samples:

- Acidity
- Alkalinity
- pH
- BOD
- COD

- Conductivity
- Total dissolved solids
- Anion analysis for $SO_4^{=}$, NO_2^{-}/NO_3^{-}, and $CO_3^{=}$
- Total suspended solids
- Dissolved oxygen
- Ammonia
- HCN

All these analyses can be performed either in the field or the laboratory using reagent test kits, although practicable considerations will usually indicate that all analyses except BOD, COD, and suspended solids will be done in the field. These kits, which are manufactured by Hach or Bausch and Lomb, use a series of procedures that usually follows a modified and simplified version of standard methods. The reagents are encapsulated and stored in small plastic pillows in pre-measured quantities until opened for analysis. Upon addition of the reagent or reagents to the sample, component concentrations are determined colorimetrically or turbidimetrically using reference color discs or portable photometers. In some cases endpoint titrations are used. Although they are not as accurate as the standard laboratory procedures, they have sufficient accuracy for Level 1 objectives and provide the following advantages which qualify them for Level 1 survey use:

- Sample preservation - The need for involved sample preservation schemes is eliminated by on-site analysis.
- Storage space - The need for large areas for sample storage is eliminated.
- Simplicity - The reagent test kits are designed to be used by non-technical personnel.
- On-site analysis - This points out specific problem areas allowing more detailed sampling by the survey team, if necessary.
- When used in the laboratory for analysis of leachables, they provide quick, inexpensive analyses for the required data.

CHAPTER VIII
LEVEL 1 ORGANIC ANALYSIS TECHNIQUES

8.1 INTRODUCTION

In order to ensure that important emission problems do not go undetected, and at the same time to allow the evaluation of a large number of sources in a cost effective manner, a simple set of analytical survey methods is presented in this chapter. Rather than to represent a comprehensive analysis, the objective of these Level 1 procedures is to provide an estimate of the predominant classes of organic compounds present in a given sample. As a result, the methodology is designed to determine the presence or absence of all major classes of organic compounds within the factor of two quantitative objectives of the Level 1 analysis. In addition, these methods can be performed in most laboratories and by a technical staff with limited previous experience.

Samples obtained in accordance with the procedures outlined in Chapters II through VI will be either gases, liquids, or solids. The multimedia analysis flow scheme presented in Figure 28 shows how each of the sample types is split for organic analysis.

8.2 LEVEL 1 ORGANIC ANALYSIS METHODOLOGY

An overview of the methodology to be used for the Level 1 organic analysis is shown in Figure 29. This methodology deals with the preparation of the samples to provide a form suitable for analysis, and with their subsequent analysis.

As indicated in Figure 29, the extent of sample preparation required varies with sample type. The low molecular weight C_1-C_6 hydrocarbons are determined by gas chromatography on site and require no preparation. Organic liquids, such as fuel oils, will not need pretreatment and are placed directly into the analysis scheme. However, the majority of the samples, including the SASS train components, aqueous solutions such as scrubber waters, and bulk solids such as coal or slag, require extraction with solvent prior to analysis. This extraction separates the organic portion of the samples from the inorganic species and allows analysis to proceed without complication. The analysis of organic extract or organic

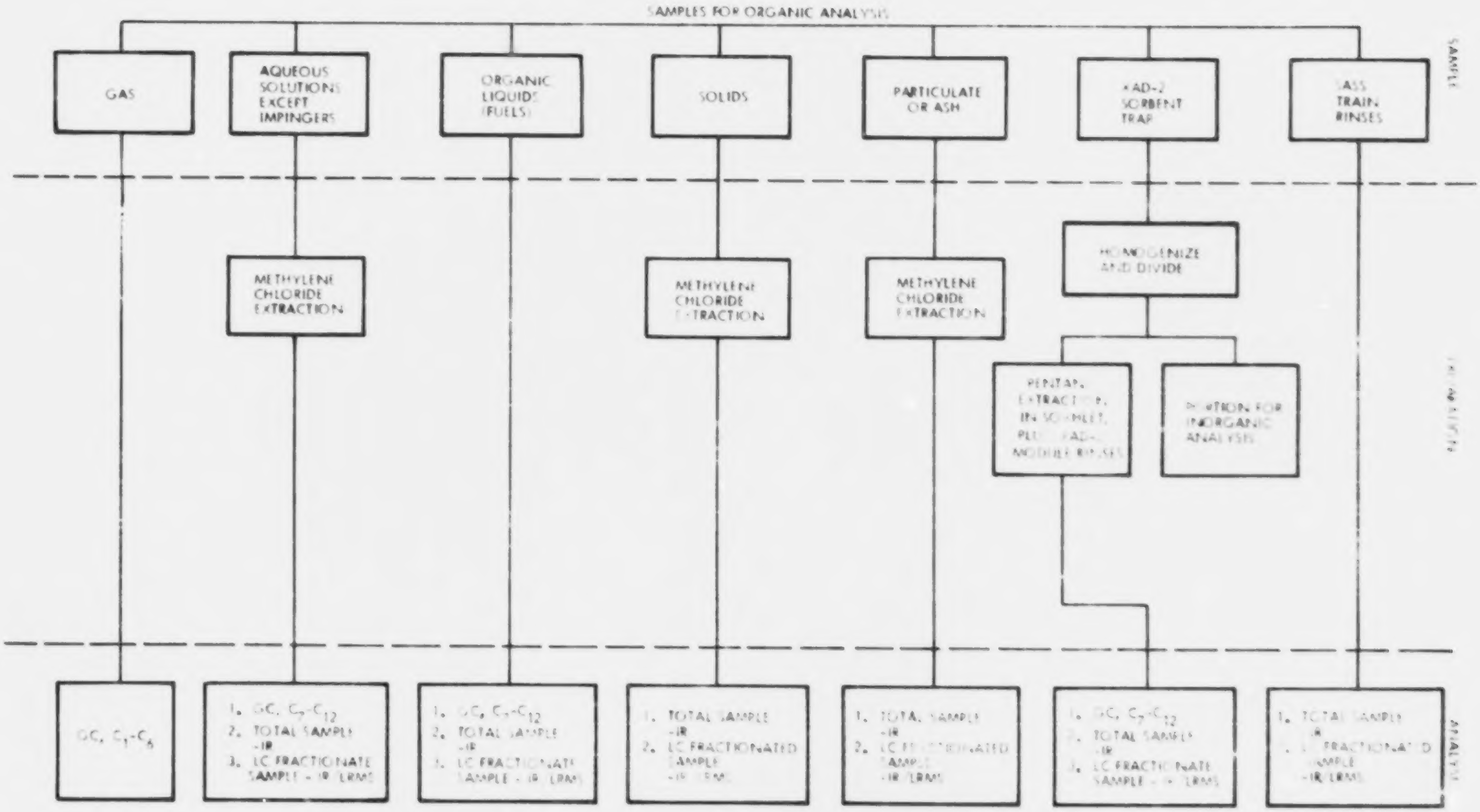

SAMPLES FOR ORGANIC ANALYSIS
SAMPLE
PREPARATION
ANALYSIS
GAS
AQUEOUS SOLUTIONS EXCEPT IMPINGERS
ORGANIC LIQUIDS (FUELS)
SOLIDS
PARTICULATE OR ASH
XAD-2 SORBENT TRAP
SASS TRAIN RINSES
METHYLENE CHLORIDE EXTRACTION
METHYLENE CHLORIDE EXTRACTION
METHYLENE CHLORIDE EXTRACTION
HOMOGENIZE AND DIVIDE
PENTANE EXTRACTION IN SOXHLET, PLUS XAD-2 MODULE RINSES
PORTION FOR INORGANIC ANALYSIS
GC, C_1-C_6
1. GC, C_7-C_{12} 2. TOTAL SAMPLE -IR 3. LC FRACTIONATE SAMPLE - IR/LRMS
1. GC, C_7-C_{12} 2. TOTAL SAMPLE -IR 3. LC FRACTIONATE SAMPLE - IR/LRMS
1. TOTAL SAMPLE -IR 2. LC FRACTIONATED SAMPLE -IR/LRMS
1. TOTAL SAMPLE -IR 2. LC FRACTIONATED SAMPLE -IR/LRMS
1. GC, C_7-C_{12} 2. TOTAL SAMPLE -IR 3. LC FRACTIONATE SAMPLE - IR/LRMS
1. TOTAL SAMPLE -IR 2. LC FRACTIONATED SAMPLE -IR/LRMS

Figure 28. Multimedia Organic Analysis Overview

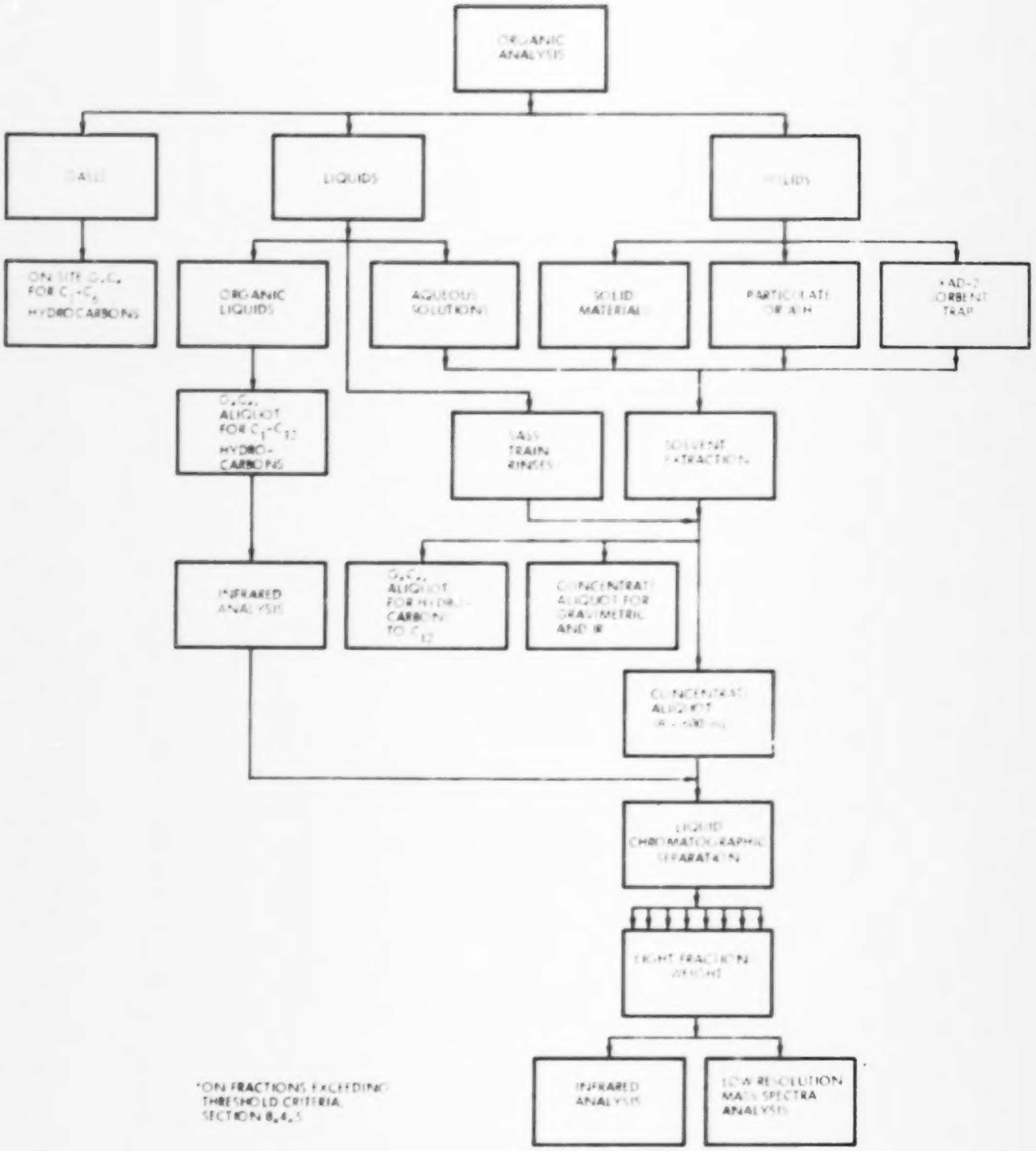

ORGANIC ANALYSIS
GASES
LIQUIDS
SOLIDS
ON SITE G.C. FOR C_1-C_6 HYDROCARBONS
ORGANIC LIQUIDS
AQUEOUS SOLUTIONS
SOLID MATERIALS
PARTICULATE OR ASH
XAD-2 SORBENT TRAP
G.C. ALIQUOT FOR C_7-C_{12} HYDROCARBONS
SASS TRAIN RINSES
SOLVENT EXTRACTION
INFRARED ANALYSIS
G.C. ALIQUOT FOR HYDROCARBONS TO C_{12}
CONCENTRATE ALIQUOT FOR GRAVIMETRIC AND IR
CONCENTRATE ALIQUOT (R < 500 mg)
LIQUID CHROMATOGRAPHIC SEPARATION
EIGHT FRACTIONS WEIGHT
INFRARED ANALYSIS
LOW RESOLUTION MASS SPECTRA ANALYSIS
*ON FRACTIONS EXCEEDING THRESHOLD CRITERIA SECTION 8.4.5

Figure 29. Level 1 Organic Analysis Flow Diagram

liquid then proceeds by first taking an aliquot of the sample or extract for direct GC analysis of compounds boiling in the range of C_7-C_{12} hydrocarbons (100-200°C). Then an infrared (IR) spectrum is obtained on the second aliquot. This IR spectrum provides an indication of the types of functional groups present in the sample and also provides a control check point for subsequent analyses. All functional groups identified in this total sample must be accounted for in the succeeding steps.

The sample extract or organic liquid is separated by silica gel liquid chromatography (LC), using a solvent gradient series, into eight fractions of varying polarity. The weight of each of these fractions is obtained so that one can determine the distribution of the sample by the various class types. An IR spectrum is then obtained on each LC fraction for determination of the types of functional groups present. A low resolution mass spectrum (LRMS) is also obtained on all fractions which exceed the concentration threshold criteria in order to determine the principal compound types present in each fraction. For the sample streams identified in the Level 1 scheme, these concentrations, computed back to the source, are:

• Gas (particulate, sorbent trap, etc.)	0.5 mg/m^3
• Solids	1 mg/kg
• Solutions	0.1 mg/l

Care must be taken in this computation to correct for those C_7-C_{12} compounds that were analyzed by GC and not lost in the LC concentration step.

It should be emphasized that sample contamination and solvent impurities are common problems in organic analysis. The best possible laboratory procedures must be used along with verified pure solvents. Blanks and controls should be run for each stage in the analysis scheme.

8.3 SAMPLE PREPARATION

This section presents sample preparation procedures that are appropriate for most samples. The specific solvents indicated should be used where possible. In the case of unusual sample requirements, an alternate procedure should be selected and presented to the project officer and the Process Measurements Branch, IERL-RTP, for approval. An aliquot of sample extracts will be set aside for direct gas chromatographic analysis of materials in the C_7-C_{12} boiling range. It is necessary to obtain the total weight of organics in the solvent extract, to obtain an IR on a portion from this extract, and to concentrate the extract for the LC separation. The appropriate stage at which to conduct each of these steps (gravimetric analysis, IR, concentrate) will depend on the quantity and solubility of the sample.

When possible, it is recommended to have at least 10 mg of sample for the gravimetric analysis. Prior to the LC analysis step, it is recommended that the solvent solutions be concentrated to 1 to 10 ml. The Kuderna-Danish apparatus for volumes less than one liter is recommended for sample concentration, and a rotary evaporator is recommended for volumes which exceed this amount.

8.3.1 Aqueous Solutions

Extraction of aqueous solutions should be carried out with methylene chloride using a standard separation funnel fitted with a Teflon stopcock. If necessary, ammonium hydroxide or hydrochloric acid should be used to adjust the pH of the water to neutral before extraction. Normally, three 500-ml methylene chloride extractions of 10-liter samples should be sufficient.

8.3.2 Solids, Particulate Matter and Ash

All solid material including products, raw materials, cyclone, probe and filter particulate, and ash should be extracted for 24 hours with methylene chloride in a Soxhlet apparatus. The Soxhlet cup must be previously extracted in order to avoid contamination. Cover the sample with a plug of glass wool during the extraction to avoid carry-over of the sample.

8.3.3 Sorbent Trap

The XAD-2 resin from the sorbent trap is extracted with pentane. After the resin is removed from the SASS train cartridge, homogenized, and a 2-g portion is removed for the inorganic analysis, the balance is extracted to remove the organic material. A large Soxhlet extraction apparatus, available from several manufacturers, must be used to extract the 400 ml of resin. The resin is then transferred to a previously cleaned extraction thimble and secured with a glass wool plug. Approximately

2 liters of pentane is added to the 3-liter reflux flask. (The dumping volume of an appropriate commercial extractor is 1500 ml.) The resin is extracted for 24 hours. The boiling pentane in the flask should be examined periodically to determine whether additional solvent is needed to replace that lost by volatilization.

If large quantities of polar materials are extracted, they may precipitate in the boiling flask near the completion of the extraction. Addition of cool methylene chloride to the flask, after extraction is complete, will simplify the subsequent transfer and analysis steps.

The XAD-2 resin should not be extracted with methylene chloride in the Soxhlet apparatus because the compatibility of this resin with methylene chloride has not been fully evaluated.

8.4 ANALYSIS OF SAMPLES FOR ORGANICS

The analysis of each of the prepared or isolated samples for organic compounds follows the scheme introduced in Figure 29. The overall scheme is based upon an initially recommended scheme (Ref. 51) which has been revised based upon subsequent laboratory evaluations (Ref. 70).

The LC/IR/LRMS procedure will provide reliable data on the compound types present in the samples for the relatively high boiling compounds. Unfortunately, the SASS train will not capture (and retain for analysis) the organic compounds with boiling points in the C_1-C_6 range (up to 70°C); and the volatile materials in the C_7-C_{12} range (100-200°C) are lost in various degrees in the sample concentration steps required for the full analysis. Consequently, separate gas chromatography procedures have been devised for the analysis of these two ranges of materials.

8.4.1 Gas Chromatographic Analysis of C_1 - C_6 Range (Ref. 71 through 75)

The on-site gas chromatographic requirements for analysis of the C_1 - C_6 gases was presented in detail in Table 5 in Chapter VII. For organic analysis the GC system should be calibrated for retention time and quantity with a C_1 - C_6 n-paraffin mixture.

The conditions recommended for this analysis are:

Column: Porapak Q, 100/120 mesh, 6'
Detector: Flame Ionization
Temperature: Isothermal at 100°C

The temperature calibration curve is prepared in the standard manner (Ref. 75). The GC system will simply be separating and analyzing mixtures of materials with a given boiling point range (and polarity in some cases), rather than individual pure compounds. The boiling points of the C_1 - C_6 hydrocarbons are:

Gas	BP (°C)
Methane, C_1	-161
Ethane, C_2	-88
Propane, C_3	-42
Butane, C_4	0
Pentane, C_5	36
Hexane, C_6	69

However, since the chromatogram peaks will represent mixtures of materials present in a certain boiling range, rather than pure, individual compounds, it is recommended that material observed in the chromatogram be reported as present in the ranges given below:

Range	BP (°C)
1	-160 to -100
2	-100 to -50
3	-50 to 0
4	0 to 30
5	30 to 60
6	60 to 90

If, from other information, it is thought that the species being analyzed are solely the C_1 - C_6 hydrocarbons, the basis of the data may be reported as such and the chromatogram peaks assigned accordingly.

8.4.2 Gas Chromatographic Analysis of C_7 - C_{12} Range

The samples used for this analysis are the methylene chloride and pentane extracts before concentration, and the neat organic liquids. Organic species boiling in the range of the C_7 - C_{12} hydrocarbons which would otherwise be lost by evaporation can be analyzed in a manner similar to that described above for the C_1 - C_6 gases. The major difference is the solvent interference and GC requirements. Even for the dilute sorbent trap extracts a flame ionization detector is sufficiently sensitive for analysis to require only a one-microliter sample.

The conditions recommended for this analysis are:

Column: 1.5% OV-101 (or SE-30) on GasChrom Q, 100/120 mesh, 1/8" OD x 6' SS

Detector: Flame ionization

Temperature Program: Isothermal at 50°C for 5 min., then program at 10°C/min to upper limit of 150°C.

The initial isothermal portion of the temperature program is required to allow the solvent to elute prior to the C_7 hydrocarbon. It will probably be desirable to prepare solutions of the neat organic liquids in order to prevent overloading and degradation of the column.

The basic calibration and reporting requirements are the same as for the C_1 - C_6 gases. The boiling points of the hydrocarbons and recommended reporting ranges are:

Vapor	BP (°C)	Range	BP (°C)
Heptane, C_7	98	7	90 to 110
Octane, C_8	126	8	110 to 140
Nonane, C_9	151	9	140 to 160
Decane, C_{10}	174	10	160 to 180
Undecane, C_{11}	196	11	180 to 200
Dodecane, C_{12}	216	12	200 to 220

Since the numbers of possible compounds in these ranges are very large, it is recommended that material and its quantity simply be reported as being present in these ranges. Any specific compound assignments should be supported by confirmatory data and may be beyond the scope of the Level 1 analysis.

8.4.3 Liquid Chromatographic Separation

The detailed procedure for the liquid chromatographic (LC) separation is given in Appendix C. All sample extracts and neat organic liquids are subjected to this procedure, if sample quantity is adequate. A 100 mg portion of the sample is preferred for the LC, but smaller quantities down to a lower limit of about 8 mg may be used. The sample is separated into approximate classes on silica gel using a gradient elution technique. The solvent sequence used for the procedure is given in Table 6.

Table 6. Solvents Used in Liquid Chromatographic Separations

Fraction No.	Solvent Composition
1	Pentane
2	20% Methylene Chloride in Pentane
3	50% Methylene Chloride in Pentane
4	Methylene Chloride
5	5% Methanol in Methylene Chloride
6	20% Methanol in Methylene Chloride
7	50% Methanol in Methylene Chloride
8	5/70/30, Conc. HCl/Methanol/Methylene Chloride

The LC separation procedure is not a high resolution technique and consequently there is overlap in class type between many of the fractions. Fraction 1 contains only the paraffins and possibly some olefins. Fractions 2 through 4 contain predominantly aromatic species. The smaller aromatics (benzene, naphthalene) will tend to elute in the early fraction (2) while the larger aromatics (benzpyrene, etc.) will tend to elute in Fractions 2 through 4. Some low polarity oxygen and sulfur containing species may also elute in Fraction 4 but most of these will not elute until addition of methanol.

Fractions 5 through 7 will contain the polar species including phenols, alcohols, phthalates, amines, ketones, aldehydes, amides, etc. The distribution of class type between Fractions 5 through 7 will be a function of their polarity and affinity for the silica gel. Some weak acids may elute in Fraction 7.

The very polar species, primarily acids such as carboxylic acids and sulfonic acids, will elute in Fraction 8.

After each fraction is collected, it should be transferred to a tared aluminum micro weighing dish for evaporation and gravimetric analysis. Fraction 8 should be dried in a glass container because of its hydrochloric acid content. Each fraction is subsequently analyzed by IR and, when the quantity is sufficient, LRMS (see Section 8.4.5).

8.4.4 Infrared Analysis

The total sample extract, or neat liquid, and the eight LC fractions are analyzed by infrared (IR) spectrophotometry. IR spectra are obtained on KBr salt plates using methylene chloride to transfer the sample to the plates. A grating spectrophotometer should be used. Sample quantity is adjusted so that the maximum signal of the strongest peaks is about 10% transmission. The transmission signal of the most intense peak should not be less than 10%.

Spectra are interpreted in terms of functional group types present in the sample or LC fraction. The many reference texts (Ref. 76 through 79) in this area are of considerable help in interpreting the IR spectra.

8.4.5 Low Resolution Mass Spectrometry

Low resolution mass spectra (LRMS) are obtained on each LC fraction which has sufficient quantity, when referenced back to the source. For the various samples those quantities are:

Gas - SASS train samples	0.5 mg/m^3
- Ambient air - particulate	1 ug/m^3
- Ambient air - Sorbent trap	0.5 mg/m^3
Solids	1 mg/kg
Aqueous solutions	0.1 mg/l

The mass spectrometer should preferably have a resolution ($m/\Delta m$) of 1000, batch and direct probe inlet, variable ionizing voltage source and electron multiplier detection. Volatile samples are analyzed by insertion in the batch inlet. It is anticipated, however, that most samples will require analysis via the direct insertion probe. A small quantity of sample is placed in the probe capillary and inserted into a cool source. The temperature is then programmed up to vaporize the sample. Spectra are recorded periodically throughout this period. Spectra are normally obtained at 70 ev ionizing voltage, but low voltage (10 ev) spectra may be much simpler in some cases. Spectra may be obtained at both high and low voltage dictated primarily by the spectra obtained.

Interpretation of the spectra is guided by knowledge of the LC separation scheme, the IR spectra, and other information about the source. Data are grouped by homologous series based on a most probable structure assignment. Molecular ion series and fragment ions help to identify compound classes. Polynuclear aromatic hydrocarbons are characterized by intense double ionization. Many other factors go into the interpretation of the spectra guided by the sample itself, experience, and literature references. The compilations of reference spectra (Ref. 80 through 83) are particularly helpful in the task of reducing the LRMS data.

CHAPTER IX

PARTICLE MORPHOLOGY AND IDENTIFICATION

9.1 INTRODUCTION

Level 1 particle morphology and identification use techniques designed to study the physical (including structure) and chemical properties of individual particles so that qualitative information concerning the potential health effects of the collected particulate matter can be determined. An environmental assessment effort generates particulate matter samples from the SASS trains and from high volume samples collecting fugitive emissions. An important part of the morphological examination of particulate matter is the identification of contributing sources, e.g., fly ash, bottom ash, coal dust, catalyst, etc., so that a detailed Level 2 particulate matter sampling effort can be planned.

The Level 1 effort described in this chapter is based on field weights and microscopic techniques which include photomicrography, particle size distribution, and polarized light micrography (PLM).

- Field weight - Preliminary weights will act as a control for contamination and/or loss of sample.
- Photomicrography - Field or laboratory photographs will provide sample control and stability checks during shipping and handling and will provide preliminary visual identification of particles and particle characteristics. (It is recommended that a color photomicrograph be taken in the field for documentation of the sample and its stability).
- Size distribution - Size distribution of fugitive emissions particulate should be determined using the photomicrograph.
- Polarized light micrography (visual identification) - Using polarized light (Ref. 84, 85, 86), the particulate matter is viewed under a microscope; particles down to 0.5μ can be identified by physical appearances.

Although the procedures described in this chapter are straightforward, they do require a degree of skill, experience and the ability to make consistent subjective evaluations on the part of the personnel performing the work. Component identification should be carried out by a trained technician and/or microscopist either internally or in a commercial laboratory specializing in the procedures described in this chapter. The same personnel or commercial laboratory should be used for each individual or series of environmental assessments. In either case, cost guidelines such as those in Reference 1 or as specified by the project officer should be followed so the cost of the microscopic analysis does not exceed its utility.

9.2 PARTICLE CHARACTERIZATION

Figure 30 presents a flow chart for the Level 1 identification and characterization of unknown particles. The tests indicated in the figure should be performed in conjunction with the macro inorganic and organic tests performed on the complete sample fractions (see Chapters VII and VIII). To obtain a maximum amount of information from a given sample, a detailed discussion of particle analysis by microscopy can be found in Ref. 84.

9.2.1 Handling Particles for Microscopic Examination

Whenever the particulate sample is handled, care must be taken to avoid contamination or mutilation. The mounting of the sample should be performed in a dust free environment. Furthermore, for sizing purposes, any manipulations that would grind or crush the sample should be avoided.

Although the mounting of particulate matter from the cyclones is straightforward, the material collected on filters, especially if matted filters are used, can cause several problems. Care must be taken to ensure that any removal process does not dislodge any of the filter material. In many cases, the quantity of particulate matter collected on the filter material may be small and difficult to remove. If a sufficient layer of particulate matter is collected so that a small (1-10mg) quantity can be scraped off, then a complete microscopic analysis can be performed. If the particles cannot be removed from the filter, only a photomicrograph for quality control and preliminary visual identification can be taken.

9.2.2 Photomicrography and Particle Sizing for Fugitive Emissions

After the particulate matter has been mounted, a color photomicrograph is taken to identify the sample and to check chemical stability. This photograph will be part of the documentation that accompanies the sample as it is logged and stored. If long periods of time occur between sampling and analysis, the original photomicrograph is compared to a recent one to determine if any physical change has occurred in the sample.

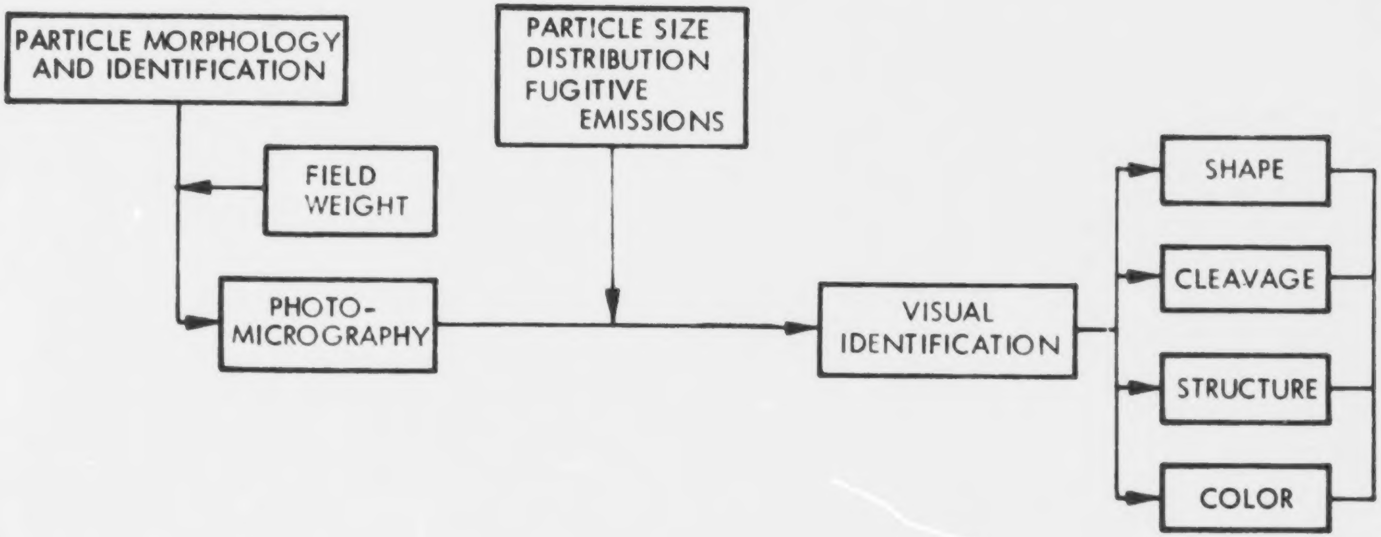

PARTICLE MORPHOLOGY AND IDENTIFICATION
FIELD WEIGHT
PHOTO-MICROGRAPHY
PARTICLE SIZE DISTRIBUTION FUGITIVE EMISSIONS
VISUAL IDENTIFICATION
SHAPE
CLEAVAGE
STRUCTURE
COLOR

Figure 30. Particle Characterization Flow Scheme

The microphotographic procedure is thoroughly discussed in Ref. 84. In all cases, the exact conditions used (lighting, magnification, mounting liquid, etc.) should be noted so future comparisons involve the same photographic conditions.

Since particles are irregularly shaped, the term "diameter" is really not applicable in descriptions of particle size. Two general approaches have been developed to approximate the measurement of this parameter. The projected diameter is the diameter of a circle equal in area to the profile of the particle when viewed normal to the positions of greatest stability (Ref. 87). The statistical diameter takes some average linear measure of the projection of the particle in a fixed direction, assuming the particles are randomly oriented (Ref. 88). Statistical diameters can be measured as the mean distance between two tangents on opposite sides of the particle image (Feret's) or the mean length of a line that intercepts the particle image and divides it into equal areas (Martin's).

The selection of the precise method of diameter measurement is not well defined. The projected diameter corresponds closely to sedimentation measurements (Ref. 88), while Feret's and Martin's diameters are slightly greater and less than the projected diameter, respectively. For a more detailed discussion of the procedures, the reader is directed to Ref. 88.

9.2.3 Visual Identification

In many cases, the trained technician can identify particulate matter by visual observations and comparison to known samples using polarized light micrography (Ref. 84). Particles are first viewed dry mounted with top lighting and the crystal shape or structure is observed. The shape, the color, and cleavage of the crystals and other visual characteristics are together used to identify or narrow the list of possible compounds.

CHAPTER X

BIOLOGICAL TESTING

10.1 INTRODUCTION

Biological testing must be considered an integral part of the phased approach to environmental assessment. Although the primary emphasis in this and related documents (Ref. 1, 2, 3, 22, 25, 27, 45, and 51) is on traditional chemical and physical tests, biological (bioassay) tests are required in order to provide direct evidence of complex biological effects such as synergism, antagonism and bioavailability. Since in most cases, this information cannot be derived from physical and chemical tests on samples consisting of complex mixtures, biological testing will be incorporated into all three levels of the phased environmental assessment. As applied to Level 1, biological testing is limited to whole sample testing which is consistent with the survey nature of this level. Biological testing on fractionated samples or on specific components of a given sample involves a certain degree of quantification that is more appropriate to Level 2 or 3 testing.

At present, specific biological test procedures have not been completely identified and, therefore, cannot be incorporated into the manual. Thus, although bioassy testing has been identified in Figures 1 and 2 (Chapter I), exact testing requirements have not been consistently delineated in the detailed flow diagrams presented in Chapters II-VI. It should also be noted that the samples size specified in Table 1 (Chapter I) may be modified when the exact biotesting procedures are identified.

The EPA's Office of Health and Ecological Effects (OHEE) is presently developing detailed bioassay requirements and test procedures, and it is expected that the initial recommendations will be available in August, 1976. Moreover, a Level 1 bioassay procedures manual similar to this manual will be issued in January, 1977. The following sections discuss the types of tests and the scope of the manpower required for the Level 1 environmental assessment. It should be noted that, although these tests indicate current thinking by OHEE, the final recommendations may be significantly expanded or reduced.

10.2 HEALTH EFFECTS BIOASSAYS

Several test procedures are currently under consideration for stream prioritization based on potential health effects; these tests include an acute toxicity (in-vitro) test, a mutagenic screening test, and a LD_{50} screening test. Although these tests do not provide a directly correlatable measure of effects on human health, they are incorporated to provide an indication of potential adverse effects, to permit semi-quantitative prioritization of samples, and to direct further health effects studies. All health effects procedures must be conducted at EPA-approved laboratories.

10.2.1 Acute Toxicity (In-vitro) Test

An estimate of the acute cellular toxicity of solids can be obtained from an in-vitro cell mortality test utilizing aveolar macrophages from rabbit lungs. The test consists of incubating the solid sample in a culture medium for 24 hours, adding the macrophages to the sample and determining the number of dead and living cells after a second incubation period. Cell mortality is determined by means of a dye exclusion technique, i.e., living cells will not incorporate the dye and are distinguishable from the dead cells which will. This test procedure requires approximately 0.5 grams of sample and 2 to 4 days for completion of a limited dose response series. Present manpower estimates are in the range of 1 to 2 man-days per series.

10.2.2 Mutagenicity (Carcinogenicity) Screening Test

The mutagenic screening test is performed according to a modification of the procedure developed by Ames and co-workers (Ref. 89, 90, 91), and is also used as a measure of the potential carcinogenicity of a sample. Three histidine deficient Salmonella typhimurim strains (TA-1535, TA-1537, and TA-1538) are used; the reversion of the strains to prototrophy indicates mutation. The three strains have defective DNA repair systems as well as defective lipopolysaccharide coats, and exhibit extreme sensitivity to observable mutational events.

The test consists of dissolving particulate matter samples in dimethylsulfoxide (DMSO), followed by exposure of the bacterial populations to the dissolved particulate material on plates using an agar overlay method. Appropriate controls, blanks, and bacterial toxicity tests are included. The test procedure requires 0.5 grams of sample and 2 to 5 days for completion of a limited dose response series. Estimated manpower requirements are approximately 2 man-days per series.

10.2.3 LD_{50} Screening Test

The LD_{50} test is used as a measure of acute toxicity in a whole animal. The test is performed by administering known levels of the sample to a small population of mice and extrapolating the mortality rate to obtain an LD_{50} value. The test procedure requires 14 days and 15 grams of sample. Manpower requirements are approximately 1 man-day. The information obtained can be supplemented by performing the mutagenic screening test described in Section 10.2.2 on urine samples and detection of toxic metabolites produced by the animal. This would add approximately 1.2 man-days to the test cost.

10.3 ECOLOGICAL EFFECTS BIOASSAYS

A number of test procedures are currently under consideration for evaluating the effect of samples on aquatic and terrestrial forms of life. These procedures will utilize selected species of animals and plants to provide an indication of the short term toxicity of samples to non-human forms of life. In addition, the tests can potentially be extended to measure bioaccumulation and entrance into the food chain.

10.3.1 Aquatic Effects

Acute toxicity tests are conducted by exposing selected aquatic species to several levels of pollutant concentration and determining the mortality rate. Fathead minnows and daphnia are widely used in assessing fresh water effects. Comparable marine organisms are the sheephead minnow and mysid shrimp. All tests require 2 to 4 days for completion. The fresh water tests require about 1.2 man-days and 40 liters of sample. The daphnia and shrimp require approximately 3-4 man hours and 10 liters of sample. These tests can also be expanded to include bioaccumulation studies by chemical tissue assay at an added cost of 6 man-days per sample.

10.3.2 Terrestrial Effects

Although simple general tests for effects on terrestrial forms of life have not been as widely developed or applied as aquatic tests, a few specific techniques are available. The measurement of ethylene produced by plants exposed to air pollutants has been used successfully to assess the health hazards of some pollutants. This test requires 4 hours and takes approximately 2 man-hours. Measurement of the O_2 consumption and CO_2 production of soil samples containing microorganisms can also be used to assess the impact of gaseous, liquid or solid samples. Such tests require 600 hours for completion and are inexpensive. Finally, exposure of a microcosm containing a number of terrestrial species (plants and animals) to samples has been used in a few instances. This test requires 20 days and manpower requirements range from 2 to 4 man-days per system.

REFERENCES

1. Hamersma, J. W., and Reynolds, S. L., "Field Test Sampling/Analytical Strategies and Implementation Cost Estimates; Coal Gasification and Flue Gas Desulfurization," EPA-600/2-76-093b, U. S. Government Printing Office, Washington, D.C., 1976.

2. Dorsey, J., C. Lockmuller, L. Johnson, and R. Statnick. "Guidelines for Environmental Assessment Sampling and Analysis Programs – Level 1." U. S. Environmental Protection Agency, Research Triangle Park, N. C. Mar 1976, 35 pp.

3. Hamersma, J. W., and Reynolds, S. L., "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," EPA Contract No. 68-02-1412, Task Order No. 3, U. S. Environmental Protection Agency, Research Triangle Park, N. C., Mar 1975, 150 pp.

4. Brenchley, D. L., Turley, D. C., and Yaime, R. G., "Industrial Source Sampling," 1st ed, Ann Arbor Science Publishers, Ann Arbor, Mi., 1973, 439 pp.

5. ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1357-57, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 291-297.

6. Clausen J., Grant, A., Moore, D., and Reynolds, S. L., "Field Sampling for Cytotoxicity Test Samples," EPA Contract No. 68-02-1412, Task Order Nos. 8, 14, 15, U. S. Environmental Protection Agency, Research Triangle Park, N. C., Sept 1975, 87 pp.

7. Bombaugh, K., Cavanaugh, E., Dickerman, J., Keil, S., Nelson, T., Cowen, M., and Rosebrook, D., "Sampling and Analytical Strategies for Compounds in Petroleum Refinery Streams," Vol. I and II, EPA Contract No. 68-02-1882, U. S. Environmental Protection Agency, Research Triangle Park, N. C., 1975.

8. Application of El Paso Natural Gas Co. before U. S. Federal Power Commission, Docket No. CP73-131, El Paso, Tx., Aug 1972.

9. Danielson, J. A., "Air Pollution Engineering Manual," 2nd ed, Air Pollution Control District, County of Los Angeles, Los Angeles, Ca., 1973, p 987.

10. Shaw, H., and Magee, E. M., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes in Gasification", EPA-650/2-74-009-C, U. S. Government Printing Office, Washington, D. C., 1974.

11. ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D1145-53, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 1208-1213.

12. ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1605-60, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 349-380.

13. ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D1247-54, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 222-231.

14. Leithe, W., "The Analysis of Air Pollutants," 1st ed, Ann Arbor-Humphrey Science Publishers, Ann Arbor, Mi., 1970, p 150.

15. U.S. Environmental Protection Agency, Federal Register 36, 24876 (1971).

16. Intersociety Committee, "Methods of Air Sampling and Analysis," 1st ed, American Public Health Association, Washington, D.C., 1972, p 480.

17. Mueller, P.K., Chairman, "Methods in Air Pollution and Industrial Hygiene Studies," 12th Conference, University of California, Los Angeles, Ca., 1971, p 170.

18. American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments," 4th ed, ACGIH, Cincinnati, Oh., 1972, pp S-1 to S-50.

19. Lapson, W.F., Dehne, H., and Harris, D.B., presented to 67th Annual Air Pollution Control Association meeting, Denver, June 1974.

20. Silverman, L., Billings, C., and First, M., "Particle Size Analysis in Industrial Hygiene," 1st ed, Academic Press, New York, N.Y., 1971, 371 pp.

21. Ahuja, S., Cohen, E., Kneip, T., Lambert, J., and Zweig, G., "Chemical Analysis of the Environment and Other Modern Techniques," 1st ed, Plenum Press, New York, N.Y., 1973, 384 pp.

22. Flegal, C. A., Starkovich, J. A., Maddalone, R. F., Zee, C., and Kraft, M. L., "Procedures for Process Measurements, Trace Inorganic Materials," EPA Contract No. 68-02-1393, U. S. Environmental Protection Agency, Research Triangle Park, N. C., July, 1975, 130 pp.

23. Geiver, P. M., in "Air Pollution," Volume II, A. C. Stern, Ed., Academic Press, New York, N. Y., 1968, p 249.

24. Deming, W. E., "Some Theory of Sampling," 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1955, 500 pp.

25. Maddalone, R. F., and Quinlivan, S. C., "Technical Manual for Inorganic Sampling and Analysis," EPA Contract No. 68-02-1412, Task Order No. 16, U. S. Environmental Protection Agency, Research Triangle Park, N. C., Apr 1976, Section 01-04.

26. ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D2928-71, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 832-858.

27. Kolnsberg, H., "Technical Manual for the Measurement of Fugitive Emissions," EPA-600/2-76-089-A, U. S. Government Printing Office, Washington, D. C., 1976.

28. Vandergrift, A., Shannon, L., Lawless, E., Borman, P., Sailee, E., and Reichel, M., "Particulate Pollutant System Study, Volume III – Handbook of Emission Properties," EPA Contract No. 22-69-104, U. S. Environmental Protection Agency, Durham, N. C., 1971, p 629.

29. ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D2682-71, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 699-710.

30. U. S. Environmental Protection Agency, Federal Register 36, 22384 (1971).

31. Seeley, J. L., and Skogerboe, R. K., Anal. Chem. 46, 415 (1974).

32. Midwest Research, Inc., and Hittman Associates & Co. "Methods for Identifying and Evaluating the Nature and Extent of Non-Point Sources of Pollutants," EPA-430/9-73-014, U. S. Government Printing Office, Washington, D.C., 1973.

33. "Handbook for Monitoring Industrial Wastewater," U. S. EPA Technology Transfer Series, U. S. Government Printing Office, Washington, D.C., 1973.

34. McCoy, J. W., "Chemical Analysis of Industrial Water," 1st ed, Chemical Publishing Co., New York, N. Y., 1969, pp 175-176.

35. Lager, J. A., and Smith, W. A., "Urban Stormwater Management and Technology – An Assessment," EPA-600/2-75-065, U. S. Government Printing Office, Washington, D.C., 1974.

36. Taras, M. J., Greenburg, A. E., Hoak, R. D., and Rand, M. C., "Standard Methods for the Examination of Water and Wastewater," 13th ed, American Public Health Association, New York, N. Y., 1971, 874 pp.

37. Shelley, P. E., and Kirkpatrick, G. A., "An Assessment of Automatic Sewer Flow Samples," EPA-600/2-75-065, U. S. Government Printing Office, Washington, D.C., 1975.

38. Sridharan, N., and Lee, G. F., J. of Water Pollution Control Assoc. 46, 684 (1974).

39. Wanielista, M. P., Yousef, Y. A., and McLellan, W. M., presented at the 48th Annual Water Pollution Control Federation Conference, Miami Beach, Fl., Oct 1975.

40. Chamberlain, T., Jones, D., Trost, J., and Grant, A., "Interim Report for Fabrication and Calibration of Series Cyclone Sampling Train," EPA Contract No. 68-02-1412, Task Order No. 7, U. S. Environmental Protection Agency, Research Triangle Park, N. C., Apr 1975, 54 pp.

41. Brookman, G. T., Martin, D. K., Bender, J. J., and Persio, J. V., "Evaluation of Waterborne Fugitive Emissions," TRC Project 32593 Task 02 Report, Wethersfield, Ct., June 1976, 151 pp.

42. ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1066-67T, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 125-135.

43. ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1192-64, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 190-195.

44. ASTM Committee D-2 and F-7, "Petroleum Products-LPG, Aerospace Materials, Sulfonates, Petrolatum, Wax," Part 18, D270-65, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 47-71.

45. Faeirheller, R., Marn, P. J., Harris, D. H., and Harris, D. L., "Technical Manual for Process Sampling Strategies for Organic Materials," EPA-600/2-76-122, U. S. Government Printing Office, Washington, D.C., 1976.

46. Gould, R.F., ed., "Coal Science," Advances in Chemistry Series 55, American Chemical Society, Washington, D.C., 1966, Sections III, IV and VI.

47. Anderson, W.W. in "Standard Method of Chemical Analysis," 6th ed, F. Welcher, Ed., D. Van Nostrand Co., Inc., Princeton, N.J., 1963, pp 28-38.

48. ASTM Committee D-3, D-5 and D-22, "Plastics-Specifications, Methods of Testing Pipe, Film, Reinforced and Cellular Plastics," 1974 Annual Book of ASTM Standards, Part 26, D2234-72, American Society for Testing and Materials, Philadelphia, Pa., 1974, pp 482-498.

49. Leonard, J.W., and Mitchell, D.R., "Coal Preparation," 3rd ed., The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, N.Y., 1968, Chapters 6, 7 and 8.

50. Lowry, H.H., ed., "Chemistry of Coal Utilization," Suppl. Vol. 1019, John Wiley and Sons, New York, N.Y., 1963, 1142 pp.

51. Jones, P., Graffeo, A., Detrick, R., Clarke, P., and Jacobsen, R., "Technical Manual for Analysis of Organic Materials in Process Streams," EPA-600/2-76-072, U. S. Government Printing Office, Washington, D.C., 1976.

52. Nicholls, G. D., Graham, A., Williams, E., and Wood, M., Anal. Chem. 39, 584 (1967).

53. Attari, A., "Fate of Trace Constituents of Coal During Gasification," EPA-650/2-73-004, U. S. Government Printing Office, Washington, D.C., 1973.

54. Ahearn, A., ed., "Trace Analysis by Mass Spectrometry," 1st ed, Academic Press, New York, N. Y., 1972, 460 pp.

55. Javorskii, F. F., Anal. Chem. 46, 2080 (1974).

56. Von Lehmden, D., Jungers, K., and Lee, R. Jr., Anal. Chem. 46, 239 (1974).

57. Kessler, T., Sharkey, A., and Friedel, R., "Spark Source Mass Spectrometer Investigation of Coal Particles and Coal Ash," Bureau of Mines Technical Progress Report 42, Pittsburgh, Pa., 1971, 15 pp.

58. Jacobs, M.L., Sweeney, S.L., and Webster, C.L., in "Keystone Coal Industry Manual," 1975 ed., G.F. Nielson, Ed., McGraw-Hill Mining Publications, New York, N.Y., 1975, pp. 243-245.

59. Brown, R., Jacobs, M.L., and Taylor, H.E., American Laboratory 4, 29 (1972).

60. Brown, R., and Taylor, H.E., "The Application of Spark Source Mass Spectrometry to the Analysis of Water Samples," Proceedings of the American Water Symposium No. 18, American Water Resources Association, Urbana, Il., 1974, p 72.

61. Bringham, K.A., and Elliott, R.M., Anal. Chem. 43, 43 (1971).

62. Guidoboni, R.J., Anal. Chem. 45, 1275 (1973).

63. Dean, J.A., and Rains, T.C., "Flame Emission and Atomic Absorption Spectrometry in Components and Techniques," Vol. 2, Marcel Dekker, Inc., New York, N.Y., 1971, Chapter 10.

64. Angino, E.E., and Billings, G.K., "Atomic Absorption Spectrometry in Geology," Elsevier Publishing Co., New York, N.Y., 1967, 144 pp.

65. "Products for Water Analysis," Hach Chemical Co., Catalog No. 11, Ames,Ia., 1974, p 50.

66. "A New Concept in Water Analysis," Bausch and Lomb Analytical Systems Division, Catalog No. 33-6070, Rochester, N.Y., 1976, p 11.

67. Czernikowski, O., American Laboratory 7, 52 (1975).

68. Patton, W.F., and Brink, A. Jr., J. Air Pollut. Control Assoc. 13, 162 (1963).

69. Dominick, D. D., "Methods for Chemical Analysis of Water and Wastes," EPA-625/6-74-003, U. S. Government Printing Office, Washington, D.C., 1974.

70. Levins, P. L., Caragay, A. B., Thrun, K. E., Stauffer, J. L., and Guilmette, L., "Evaluation of Alternative Level 1 Organic Analysis Methods," Draft Report on EPA Contract No. 68-02-2150, U. S. Environmental Protection Agency, Research Triangle Park, N. C. June 1976, pp 1-8.

71. Leibrand, R.J., Applications Laboratory Report 1006, Avondale, Pa., Mar 1966.

72. "Liquid Phase and Solid Support Applications to Chromatographic Separation," Hewlett-Packard Applications Laboratory, Avondale, Pa., 1970, 67 pp.

73. Snyder, L.R., Anal. Chem. 33, 1527 (1961).

74. "Compilation of Gas Chromatographic Data," ASTM Data Series, Publication No. DS25A, American Society for Testing and Materials, Philadelphia, Pa., 1967.

75. ASTM Committee D-2, "Petroleum Products-LPG, Aerospace Materials, Sulfonates, Petrolatum, Wax," 1971 Annual Book of ASTM Standards, Part 17, D2887-70T, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp 1072-1081.

76. Rao, C.N.R., "Chemical Applications of Infrared and Raman Spectroscopy," 1st ed, Academic Press, London, England, 1963, 683 pp.

77. Colthup, N.B., Lawrence, H.D., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy," 1st ed, Academic Press, London, England, 1964, 511 pp.

78. Cross, A.D., "An Introduction to Practical Infrared Spectroscopy," 1st ed, Butterworth, Inc., Washington, D. C., 1964, 86 pp.

79. Kendall, D.N., "Applied Infrared Spectroscopy," 1st ed, Reinhold Publishing Corporation, New York, N.Y., 1966, 560 pp.

80. Reed, R.I., "Applications of Mass Spectrometry to Organic Chemistry," 1st ed, Academic Press, New York, N.Y., 1966, 256 pp.

81. Budzikiewicz, H., Djerassi, C., and Williams, D., "Mass Spectrometry of Organic Compounds," 1st ed, Holden Day, Inc., San Francisco, Ca., 1976, 690 pp.

82. Imperial Chemical Industries, Ltd., "Eight Peak Index of Mass Spectra," 1st ed, Mass Spectrometry Data Center, Alder Maston, Reading, United Kingdom, 1970.

83. "Selected Mass Spectral Data," API Research Project No. 44, Texas A&M University, College Station, Tx., 1975.

84. McCrone, W.C., Drafty, R., and Dilly, J.C., "The Particle Atlas," 1st ed, Ann Arbor Science Publishers, Ann Arbor, Mi., 1967, 406 pp.

85. West, P.W., *The Chemist Analyst 34*, 76 (1945).

86. West, P.W., *The Chemist Analyst 35*, 4 (1946).

87. Herdon, G., "Small Particle Statistics," 2nd ed, Academic Press, New York, N.Y., 1960, 520 pp.

88. Orr, C., and Dalla Valle, J.M., "Fine Particle Measurement, Size, Surface and Pore Volume," 1st ed, Macmillan Publishing Co., New York, N.Y., 1960, p 83-91.

89. Ames, B.W., Gurney, E.G., Miller, J.A. and Bartsch, H., *Proc. Nat. Acad. Science 69*: 3128 (1972).

90. Ames, B.W., Lee, F.D. and Durston, W.E., *Proc. Nat. Acad. Science 70*: 782 (1973).

91. Ames, B.W., Durston, W.E., Yamasaki, E. and Lee, F.D., *Proc. Nat. Acad. Science 70*: 2281 (1973).

APPENDIX A

DESIGN AND PREPARATION OF A FIELD TESTING UNIT
(REFERENCES 1, 3, 6)

Mobile laboratories in the form of vans or trailers have been used very effectively for a variety of source assessment efforts such as stack sampling, ambient air sampling and water quality measurements. Because the use of a van as a mobile laboratory for on-site analysis is very desirable for the Level 1 effort, this appendix is included to aid those contractors interested in outfitting their own vans.

A.1 ADVANTAGES

In order to sample a proposed site in a timely and efficient manner, it is desirable to fabricate a field testing unit which is completely outfitted with all necessary equipment required for Level 1 sampling and on-site analysis. In addition to the obvious advantages with respect to sampling, a major advantage of such units lies in the fact that many samples may be or are unstable, and delaying the analysis could result in erroneous conclusions. In addition, the results for a given sample are often quite unexpected and the presence of an on-site laboratory allows the immediate re-analysis of a check sample and/or modification of the experimental plan on a real time basis, which allows the saving of time, effort and cost.

In the phased sampling effort for environmental assessment, many effluent parameters must be determined on-site due to their unstable nature. In addition, the philosophical aims of Level 1 testing in the phased approach can be enhanced greatly with an on-site laboratory. A well-equipped laboratory will allow additional Level 1 or "Semi-Level 2" samples to be taken so that the final Level 2 effort can be focused in greater detail, with a resultant decrease in cost for the Level 2 effort. Finally, unanticipated problem areas can be identified in greater detail for the Level 2 effort.

Most sampling efforts will require the rental of a van or trailer to transport needed equipment, tools and reagents from the laboratory to the sampling source. Driver and mileage rates must also be figured into the overall cost. Since the above costs are incurred as a natural outgrowth of most sampling efforts, the cost effectiveness of a mobile laboratory unit is greatly enhanced since these normally incurred costs may be applied to the mobile laboratory unit. An additional advantage is that sampling equipment assembly, sample transfer and equipment clean-up are facilitated by the additional work space made available in the mobile laboratory unit for all phases and types of sampling operations.

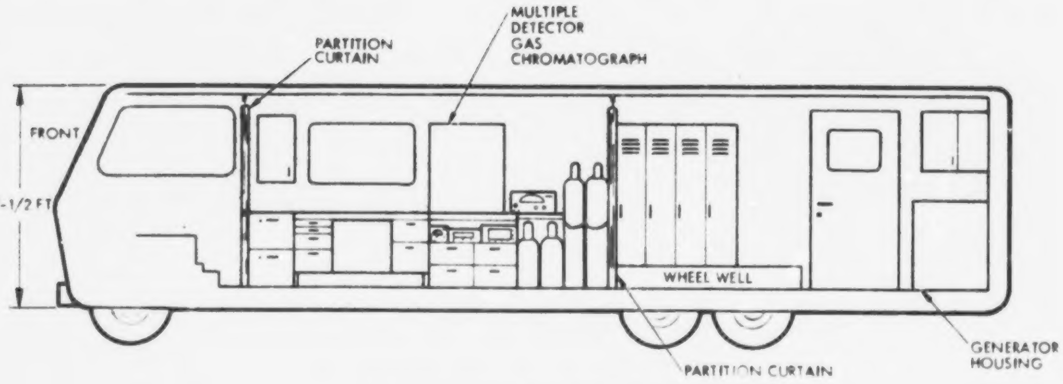
A.2 COMPONENTS AND LAYOUT

This section describes the components and layout of a Level 1 sampling and on-site analysis room. A van was chosen as the room because of the versatility and mobility of the van compared to a trailer, particularly when many sites must be visited. The discussion below, however, also applies to the outfitting of a trailer.

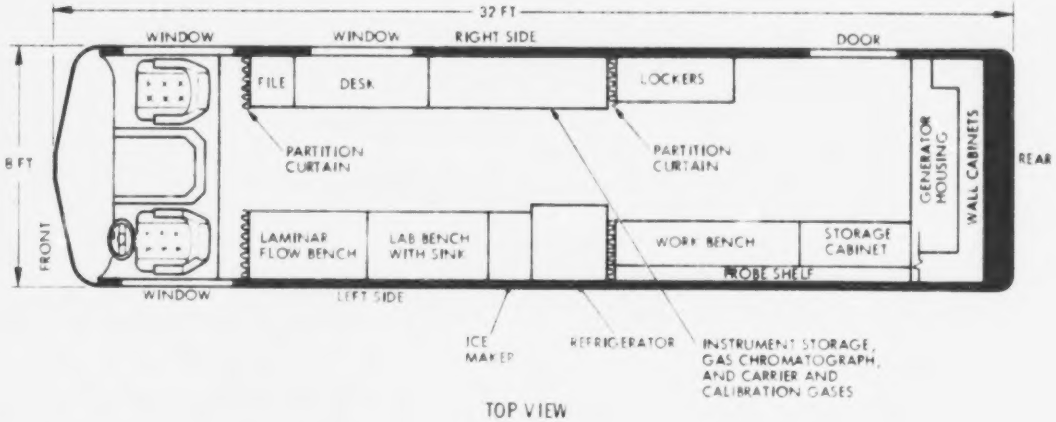
Basic furnishings of the Level 1 vans should include:

- A refrigerator for storing ice and preserving water samples.
- An ice maker to provide a continuous and convenient supply of ice for cooling down the SASS train impingers.
- Cabinets, drawers and shelves for storage of sampling equipment, tools, hardware, spare parts, glassware, sample bottles, reagents, etc.
- Work surfaces for assembling equipment and performing analyses.
- Lockers for storage of rain gear, goggles, overalls, etc.
- A desk and 2-drawer file for storage of data, notebooks and instrument and equipment manuals.
- A laminar flow bench for performing operations such as sample transfers (particularly those for trace analyses and toxicity testing) that are susceptible to ambient contamination.

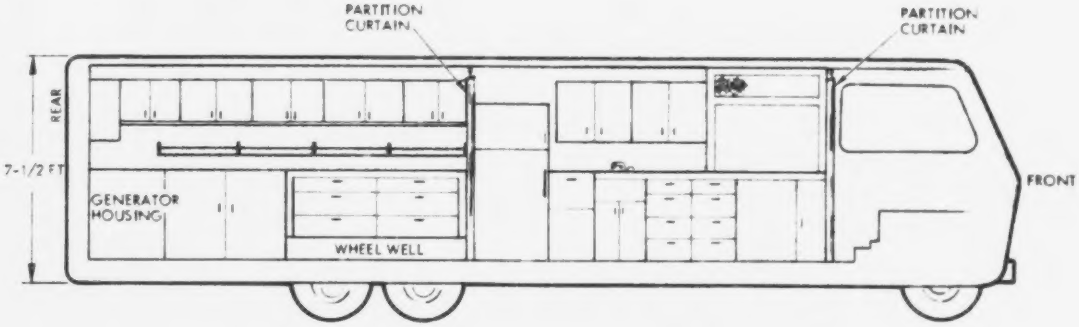
The work areas of the vans will be separated into two general areas: one for "clean" operations which will be away from the door and separated by curtains, and one for "dirty" operations. A layout design for the furnishings listed above is shown in Figure 31. Along with the basic floor plan, cutaway views of the two side walls are also presented.



CUTAWAY VIEW SHOWING RIGHT SIDE



TOP VIEW



CUTAWAY VIEW SHOWING LEFT SIDE

Figure 31. Level 1 Multimedia Mobile Laboratory

Several important criteria dealing with functionality and structural strength are incorporated in the design of the field test vans shown in Figure 31. These criteria are:

Functionality

- Maximize work surfaces and storage space.
- Separate clean work areas from dirty work areas.
- Place related supplies, equipment and work areas in close proximity.

Structural Strength and Safety

- Distribute weight evenly from side to side.
- Place heaviest load between axles.
- Avoid installing items that would require bolts into housing over a generator.

Figure 31 shows an 8' x 32' van with a 15 KW generator to support the basic van systems such as air conditioning, lights, refrigerator, ice maker, and gas chromatograph. For a completely independent power supply to support all van and sampling (SASS train) systems, a 30 KW towable diesel generator is required. Items shown in the layout are all flexible in size and design and can be chosen and assembled to make maximum usage of the space inside the van. For example, the work bench and storage cabinet at the rear of the van can be adjusted to the same height as the generator housing shelf to provide a continuous, level work surface with wall cabinets providing additional storage. Good use can also be made of the areas over the wheel wells since certain items can be built around or over the wells.

Equipment for the Level 1 mobile test van is shown in Table 7.

Additional equipment which would be used for Level 2 source assessments consists of high-accuracy, continuous monitors for particulate matter and individual gases (i.e., CO, NO_x, SO_x, O_2, and CO_2); automatic, compositing water samplers with flow monitors; high-accuracy water analysis instruments; and other special capital equipment appropriate for field use. This Level 2 sampling and analysis equipment can be carried in the vans when space and

Table 7. Level 1 Mobile Van Equipment

Gas Sampling
SASS Train
Hi-Vol Ambient Samplers
Glass bulbs with a diaphragm vacuum pump for evacuation
Gas Analysis
Multiple column and detector gas chromatograph for CO, SO_x, N_2, CO_2, O_2, C_1 - C_6 hydrocarbons, NH_3, HCN, $(CN)_2$
Water Sampling
Portable Hach Sampling Kit
Positive displacement pump and hoses
Portable flow monitoring devices
Water Analysis
Electrodes and meters to measure pH, conductivity, turbidity, and dissolved oxygen
Portable water analyzer to perform alkalinity, hardness and COD analysis
Portable Hach Analysis Kit

weight capacities permit. The excess can be drop-shipped or placed in a separate trailer as appropriate. However, the cost, bulk and weight of the equipment along with the infrequency of its use make permanent installation in the vans impractical.

APPENDIX B

PROCESS DATA NEEDS

Table 8 delineates the process data needs for a phased environmental assessment. These needs are subcategorized for plant characterization, plant operating conditions, plant stream conditions, and sampling/analysis.

Table 3. Process Data Needs for Phased Environmental Assessment

	Plant Characterization
Type of industry	Metallurgical, petro-chemical, etc.
Industrial sub-category	Type of process used
Geographical location	Urban, rural, population center, etc.
Plant boundaries	Diagram of plant and property lines showing equipment locations
Plant access	Rail, road and water connections
Products	Marketable results of plant operation
Waste products	By-products or process control wastes
Patent situation	To avoid sampling in sensitive areas
Potential health hazards	Follow OSHA and FDA guidelines
	Plant Operating Conditions
Designed plant capacity	Output at design load
Current operating load	Percentage of design load
Maximum plant capacity	Potential maximum capacity
Plant start-up	Time required to reach optimum conditions and change in stream composition during this period

Table 8. Process Data Needs for Phased Environmental Assessment (Continued)

	Plant Operating Conditions
Plant shutdown	Time required to shut down and effect on-stream compositions
Cyclic nature of process	Process condition changes (temperature, pressure and composition) with time
	Plant Stream Conditions
Process flow diagram	Overall relation of streams
Raw material streams	Location, composition, physical characteristics
Product streams	Location, composition, physical characteristics
Waste streams	Location, composition, physical characteristics
Control equipment	Type and location
Physical parameters	Temperature, pressure and flowrate
Special materials or construction	Need for specialized sampling equipment
	Sampling/Analysis
Streams to be sampled	Select representative streams
Potential sampling sites	Select potential sites on basis of above information
Availability of process instrumentation	Find on-site equipment and note condition

Table 9. Process Data Needs for Phased Environmental Assessment (Continued)

Sampling/Analysis	
Availability of utilities	Electrical and water requirements for sampling and analysis equipment
Available equipment	On-site sampling or analysis equipment
On-site laboratory support	Analytical capabilities

APPENDIX C

LIQUID CHROMATOGRAPHY SEPARATION PROCEDURE

Column: 200 mm x 10.5 mm ID, glass with teflon stopcock.

Adsorbent: Davison Silica Gel, 60-200 mesh, Grade 950, (Fisher Scientific Company). This adsorbent is activated at 110°C for two hours just prior to use. Cool in a desiccator.

C.1 PROCEDURE FOR COLUMN PREPARATION

Dry pack the chromatographic column, plugged at one end with glass wool, with 6.0 grams of freshly activated silica gel. A portion of properly activated silica gel weighing 6.0 ±0.2 g occupies 8 ml in a 10 ml graduated cylinder. Vibrate the column for a minute to compact the gel bed. Pour pentane into the solvent reservoir positioned above the column and let the pentane flow into the silica gel bed until the column is homogeneous throughout and free of any cracks and trapped air bubbles*. The total height of the silica bed in this packed column is 10 cm. The solvent void volume of the column is 2 to 4 ml. When the column is fully prepared, allow the pentane level in the column to drop to the top of the silica bed so that the sample can be loaded for subsequent chromatographic elution.

C.2 PREPARATION OF THE SAMPLE

At room temperature evaporate the solvent from an aliquot of solution containing at least 20 to 500 mg of sample. The preferred sample weight is 100 mg. Weigh this sample in a glass weighing funnel. In order to facilitate transfer of the sample, add 0.5 to 1.0 g of activated silica gel to the sample and carefully mix this with the sample using a micro-spatula.

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*A convenient device for the elimination of gel bed cracks and air bubbles is acetone coolant, which is subsequently referred to as the ACE B method. It consists of a paper towel wound loosely around the glass column along the region of the crack or bubble; the paper towel is periodically moistened with acetone. The acetone evaporation cools the region and dissipates the bubble or crack.

Table 9 shows the sequence for the chromatographic elution. In order to ensure adequate resolution and reproducibility, the column elution rate is maintained at 1 ml per minute.

Table 9. Liquid Chromatography Elution Sequence

No. Fraction	Solvent Composition	Volume Collected
1	Pentane	25 ml
2	20% Methylene chloride in pentane	10 ml
3	50% Methylene chloride in pentane	10 ml
4	Methylene chloride	10 ml
5	5% Methanol in methylene chloride	10 ml
6	20% Methanol in methylene chloride	10 ml
7	50% Methanol in methylene chloride	10 ml
8	Conc. HCl/Methanol/Methylene chloride (5 + 70 + 30)	10 ml

C.3 LOADING SAMPLE ON THE COLUMN

Quantitatively transfer the sample into the column via the weighing funnel used for sample preparation; a micro-spatula can be used to aid in the sample transfer. Rinse the funnel* with a few ml of pentane to complete the quantitative sample transfer. (Note: Do not rinse with methylene chloride because this solvent will cause the aromatics to elute with the paraffins.) Add the solvent slowly to minimize disturbing the gel bed and eliminate the trapped air bubbles, particularly in the zone of the sample-containing silica gel, by using the ACE B approach (see footnote, preceding page). The chromatographic system is now ready for sample fractionation.

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*Save this weighing funnel for subsequent additional rinsing with the solvents used at interim fractions up to methylene chloride.

C.4 CHROMATOGRAPHIC SEPARATION INTO 8 FRACTIONS

The volume of solvents shown in Table 9 represents the solvent volume collected for that fraction. If the volume of solvent collected is less than volume actually added due to evaporation, add additional solvent as necessary. In all cases, however, the solvent level in the column should be at the top of the gel bed, i.e., the sample-containing zone, at the end of the collection of any sample fraction.

After the first fraction is collected, rinse the original sample weighing funnel with a few ml of the Fraction Number 2 solvent (20% methylene chloride/pentane) and carefully transfer this rinsing into the column. Repeat as necessary for Fractions 3 and 4.

APPENDIX D

PREPARATION OF XAD-2 RESIN

The XAD-2 resin to be used in the SASS train sorbent trap must be cleaned prior to use. The resin as obtained from Rohm and Haas is soaked with an aqueous salt solution. This salt solution plus residual monomer and other trace organics must be removed before the resin can be used for sampling trace organics.

Transfer the resin to a large Soxhlet extractor with a 1.5-liter dumping volume. This requires 2 to 2.5 liters of solvent in the 3-liter supply flask. The XAD-2 resin is then extracted in sequence with the following solvents and times:

- Water - 22 hrs,
- Methanol - 22 hrs,
- Anhydrous ether - 8 hrs,
- Pentane - 22 hrs.

The water removes the salt solution and any water soluble organic material. Methanol removes the residual water from the resin and ether removes the majority of the polar organic material. Pentane is used as the final stage because it is the solvent used in the actual extraction of collected material from the resin.

After the final pentane extraction, transfer the XAD-2 resin into a clean flask and dry it under a vacuum for 18 hrs using mild heat from a heat lamp.